REGISTERED No. BG. 315

THE UNIV. OF MICH.
MAR 8 1962
PHYSICS LIBRARY

PROCEEDINGS
OF THE
INDIAN ACADEMY
OF SCIENCES

VOL. LIV] *SECTION A* [No. 6

DECEMBER 1961

Price Rs. 2 or 3 Sh. *Annual Subscription Rs. 18*

IMPORTANT

Notice to the Subscribers of the "Proceedings of the Indian Academy of Sciences"

As from 1st January 1962, the following subscription prices for the *Proceedings of the Indian Academy of Sciences* will come into effect:—

Annual Subscription Rates

	Sections A & B	Section A	Section B
Inland ..	Rs. 72 00 nP.	Rs. 36 00 nP.	Rs. 36 00 nP.
Foreign ..	$ 18 00 cts.	$ 9 00 cts.	$ 9 00 cts.
	or	or	or
	£ 6-0-0	£ 3-0-0	£ 3-0-0

The *Proceedings of the Indian Academy of Sciences*, a monthly, which commenced its publication in July 1934 in two Sections, A and B, comprising of papers in physical and biological sciences respectively, has since then maintained an unbroken record of punctual issue on the last date of every month. Two volumes in each Section are issued every year and the 54th volume is now running. Each volume contains between pages 350 to 400 of text, 15 to 20 full-page plates and a large number of figures in the text. The *Proceedings* embody the results of the scientific research of the highest quality carried out in India.

The subscription price, which was originally fixed in July 1934, has remained unaltered all these years. The printing costs have progressively increased and are at present nearly three times the original ones. It has therefore become inevitable that the subscription rates are enhanced to enable the *Proceedings* to continue to offer to our subscribers the same volume of material and the same quality of paper, printing and illustrations as at present.

PRINTED AT THE BANGALORE PRESS, BANGALORE CITY, BY T. K. BALAKRISHNAN, SUPERINTENDENT, AND PUBLISHED BY THE INDIAN ACADEMY OF SCIENCES, BANGALORE

T

Th
sul
So
the
Re
of
l

spi
sp
l

Sr
ot
th

De

THE NUCLEAR MAGNETIC RESONANCE SPECTRA OF FOUR SPIN SYSTEMS

III. Proton Resonance Spectra of α, β and γ Picolines*

BY B. D. NAGESWARA RAO‡

(Department of Physics, Muslim University, Aligarh)

AND

PUTCHA VENKATESWARLU, F.A.SC.

(Department of Physics, Indian Institute of Technology, Kanpur)

Received October 31, 1960

ABSTRACT

The ring proton resonance spectra of α, β and γ picolines have been studied at 40 Mc./sec. The spectra which belong to the classes ABCX, ABXY and A_2X_2 respectively have been completely analyzed to determine all the involved parameters.

1. INTRODUCTION

THE proton resonance spectra of pyridine and some deuterated and methyl substituted pyridines were studied earlier by Baker[1] and Bernstein and Schneider,[2] at low resolution (about 1 in 10^7). These spectra were not therefore completely analyzed to obtain the values of all the parameters. Recently Schneider, Bernstein and Pople[3] have studied again the spectra of pyridine and some deuterated pyridines under high resolution (about 1 in 10^8) and determined all the parameters by an exact analysis.

With a view to obtain accurate values of the chemical shifts and the spin-spin coupling constants involved, we have studied the proton resonance spectra of α, β and γ picolines at 40 Mc./sec. under a resolution of about 1 in 10^8. The analyses of these spectra are presented in this paper.

2. EXPERIMENTAL

The samples of α, β and γ picolines were kindly provided by Dr. H. Sripathi Rao, Central Fuel Research Institute, Jealgora. Slight traces of other isomers and some absorbed moisture are the probable impurities in the samples.[4] The spectra were obtained on a V-4300 B Varian High

* This paper is based on part of a thesis submitted by B. D. Nageswara Rao for a Ph.D. Degree of Muslim University, Aligarh.

‡ Senior Research Fellow of the Council of Scientific and Industrial Research.

Resolution NMR Spectrometer. The general experimental details were given in an earlier publication.[5]

The resonance of methyl protons, which occurs at a higher field than that of the ring protons, does not show any splitting in all the three cases studied indicating that the coupling of the ring protons with the methyl protons is small. The ring proton resonance spectra of α, β and γ picolines are reproduced in Figs. 1 (*a*), 3 (*a*) and 5 (*a*) respectively. A comparison of these spectra with the spectra of pyridine and deuterated pyridines obtained by Schneider *et al.* and a measurement of the areas enclosed under different groups of lines show that the spectra fall into the classes ABCX, ABXY and A_2X_2 respectively in the usual notation,[6] A, B, C, etc., referring to the different ring protons in the molecules as shown in Figs. 2, 4 and 6 respectively. The values of the chemical shifts (δ) for different protons in these molecules with reference signals of water, used as an external standard, are given in Table I.

TABLE I

Values of the chemical shifts (δ) for the different protons† in α, β and γ picolines with reference to the signal from water*

α-picoline		β-picoline		γ-picoline	
Type of proton	δ in p.p.m. (± 0·02)	Type of proton	δ in. p.p.m. (± 0·02)	Type of proton	δ in p.p.m. (± 0·02)
A	−1·70	A	−2·22	A	−1·83
B	−1·69	B	−1·97	X	−3·37
C	−2·12	X	−3·33	CH_3	3·09
X	−3·26	Y	−3·33	..	..
CH_3	2·81	CH_3	3·09	..	..

* The values are all corrected for bulk diamagnetic susceptibility. The susceptibility values were evaluated with the help of Pascal's constants.

† A, B, etc., denote the different protons in α, β and γ picolines as shown in Figs. 2, 4 and 6 respectively.

3. α-PICOLINE

The zero order eigenfunctions and the corresponding diagonal matrix elements for the ABCX system are given in Table I of I[5], and the non-vanishing off-diagonal elements are given in equation (2) of I. A complete solution

of the secular equation requires the diagonalization of four 3×3 matrices and hence it is not usually possible to obtain expressions for the transition energies in explicit form. The analysis cannot therefore be done in a straightforward manner.

A comparison of the group of lines due to X proton at the lower field (Fig. 1) with that due to the *ortho*-protons in pyridine[3] shows that the multiplet structure of this group remains practically unchanged, and the mutual separations between these lines are also nearly the same. This indicates firstly that the coupling between the *ortho*-protons in pyridine is small (this was actually found to be so by Schneider *et al.*) and secondly that the values of the coupling constants J_{AX}, J_{BX} and J_{CX} in α-picoline do not differ much from the corresponding values in pyridine. In view of this and the general observation that the coupling constants are not much sensitive to substitution, it was expected that a calculation of the spectrum on the basis of the corresponding parameters in pyridine* would be of help for the analysis. These parameters, expressed in cycles per second, are

$$\left.\begin{aligned} \nu_A - \nu_B &= 0 \\ \nu_A - \nu_C &= -15 \end{aligned}\right\} \qquad \left.\begin{aligned} J_{AC} = J_{BC} &= 7{\cdot}5 \\ J_{AB} &= 1{\cdot}6 \\ J_{AX} &= 5{\cdot}5 \\ J_{BX} &= 0{\cdot}9 \\ J_{CX} &= 1{\cdot}9 \end{aligned}\right\} \qquad (1)$$

Though the spectrum, thus calculated, does not fit in with the observed spectrum correctly, a general resemblance between the two was observed, which furnishes an idea about the probable positions of different transitions in the spectrum. It may be easily noted, from the large number of transitions involved, that there are several unresolved lines in the observed spectrum.

Using these calculations as a starting-point an attempt has been made to assign the lines in the observed spectrum to particular transitions, by trial and error. The following points are of considerable help in deciding upon a proper assignment.

As the off-diagonal elements in a matrix are applied adiabatically in the process of diagonalization (*a*) the trace of the matrix remains the same and (*b*) the diagonal elements will not cross each other. If we express the

* The values of the chemical shifts are also chosen to be the same, in the first instance, as methyl substitution is not expected to alter these drastically.

frequency of a transition between states $m \rightarrow n$ as $\nu_{mn} = E_n - E_m$, using the above rules we get the following relations for the ABC transitions.*

$$\left.\begin{aligned} \nu_{21} + \nu_{31} + \nu_{41} &= \Sigma\nu_A + \Sigma J_{AB} + \tfrac{1}{2}\Sigma J_{AX} \\ \nu_{95} + \nu_{10,5} + \nu_{11,5} &= \Sigma\nu_A + \Sigma J_{AB} - \tfrac{1}{2}\Sigma J_{AX} \\ \nu_{15,6} + \nu_{15,7} + \nu_{15,8} &= \Sigma\nu_A - \Sigma J_{AB} + \tfrac{1}{2}\Sigma J_{AX} \\ \nu_{16,12} + \nu_{16,13} + \nu_{16,14} &= \Sigma\nu_A - \Sigma J_{AB} - \tfrac{1}{2}\Sigma J_{AX} \end{aligned}\right\} \quad (2)$$

where

$$\left.\begin{aligned} \Sigma\nu_A &= \nu_A + \nu_B + \nu_C \\ \Sigma J_{AB} &= J_{AB} + J_{BC} + J_{AC} \\ \Sigma J_{AX} &= J_{AX} + J_{BX} + J_{CX} \end{aligned}\right\}. \quad (3)$$

And for the X transitions we get

$$\left.\begin{aligned} \nu_{51} &= \nu_X + \tfrac{1}{2}\Sigma J_{AX} \\ \nu_{16,15} &= \nu_X - \tfrac{1}{2}\Sigma J_{AX} \\ \nu_{92} + \nu_{10,3} + \nu_{11,4} &= 3\nu_X + \tfrac{1}{2}\Sigma J_{AX} \\ \nu_{12,6} + \nu_{13,7} + \nu_{14,8} &= 3\nu_X - \tfrac{1}{2}\Sigma J_{AX} \end{aligned}\right\}. \quad (4)$$

If the transitions occurring in equations (2) and (4) are assigned to the lines in the observed spectrum, $\Sigma\nu_A$, ν_X, ΣJ_{AB} and ΣJ_{AX} can easily be obtained, of which $\Sigma\nu_A$ and ν_X depend on the choice of origin in the observed spectrum.†

After the twelve transitions ν_{21}, ν_{31}, etc., in equation (2) were assigned, all the energy levels were computed from the assigned frequencies of these transitions. The remaining eighteen transitions in the ABC spectrum were then calculated and checked with the observed frequencies. The intensities of the corresponding transitions in the theoretical spectrum obtained with the parameters in equation (1) are of help in making this comparison. The agreement between the observed and calculated spectra corresponding to these eighteen transitions forms a check on the assignment of the transitions ν_{21}, ν_{31}, etc.

---

* This type of procedure has been used earlier by Fessenden and Waugh[7] in the analysis of ABC spectra.

† The value of $\Sigma\nu_A$ can, however, be utilised to find the position of $\frac{1}{3}\Sigma\nu_A$ in the observed spectrum. This position may then be fixed as a new origin to express all the transition frequencies in the theoretical and experimental spectra.

Once the observed spectrum is satisfactorily accounted for, the problem would then be to deduce the values of the involved parameters from the energy values. As this cannot be carried out by analytical methods, a numerical method was followed. Different sets of values, for all the parameters were chosen, within reasonable range around the corresponding values in pyridine (also noting the values of ΣJ_{AB} and ΣJ_{AX} which are known) and the resulting energy levels were calculated for all the sets of values. Finally, the set of values which yield energy values close to those corresponding to the above assignment were chosen as the proper set. These values, in cycles per second, are given below:

$$\left.\begin{array}{ll} \nu_A - \nu_B = 0{\cdot}5 & J_{AB} = 1{\cdot}0 \\ \nu_B - \nu_C = -17{\cdot}0 & J_{BC} = 7{\cdot}4 \\ & J_{AC} = 7{\cdot}4 \\ & J_{AX} = 4{\cdot}5 \\ & J_{BX} = 0{\cdot}6 \\ & J_{CX} = 2{\cdot}0 \end{array}\right\} . \qquad (5)$$

It may be noted that the energy values are considerably sensitive to small changes in the values in equation (5), and therefore, it cannot be said that these values represent the best for *all* the eight parameters. Further refinement of these parameters is discouraged by the presence of several

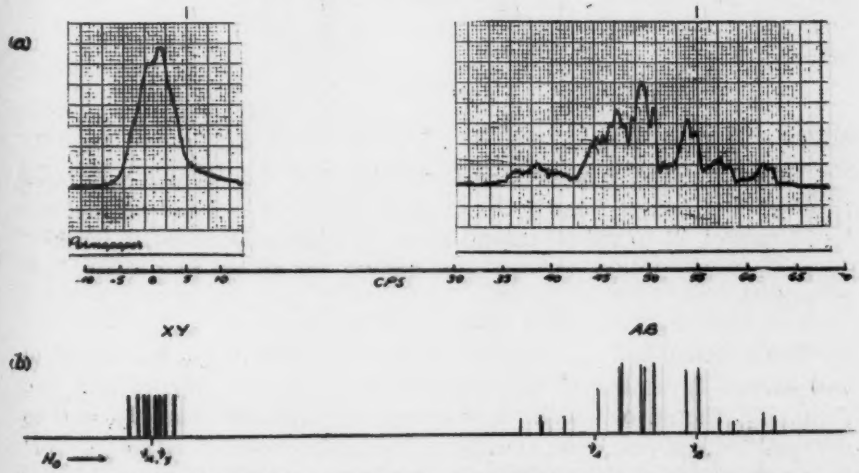


FIG. 1. H^1 NMR spectrum of α-picoline at 40 Mc./sec. (*a*) Experimental; (*b*) Calculated. X spectrum: 1 cm. =7·636 cps. ABC spectrum: 1 cm. =4·028 cps.

unresolved lines in the spectrum. The error involved in these values may be about $\pm 0{\cdot}5$ cps.

The calculated transition frequencies and relative intensities are given along with the observed frequencies in Table II. The calculated spectrum is shown in Fig. 1 (*b*).

4. β-PICOLINE

The zero order eigenfunctions and the corresponding matrix elements for the ABXY system can be easily obtained from those for the ABCX system (Table I of I[5]) by replacing C and X by X and Y respectively. The non-vanishing off-diagonal elements are given by the following relations:

$$\left.\begin{aligned} H_{25} &= H_{7,11} = H_{8,10} = H_{12,15} = \tfrac{1}{2} J_{XY} \\ H_{34} &= H_{78} = H_{10,11} = H_{13,14} = \tfrac{1}{2} J_{AB} \end{aligned}\right\} \qquad (6)$$

and the remaining elements are given by the condition

$$H_{mn} = H_{nm}$$

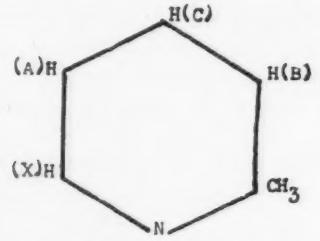


FIG. 2. α-picoline.

Now the complete spin matrix factors into four 1×1 (states 1, 6, 9 and 16), four 2×2 (states 2 and 5, 3 and 4, 12 and 15 and 13 and 14) and one 4×4 (states 7, 8, 10 and 11) sub-matrices. Explicit expressions, in terms of the parameters involved, can easily be derived, for all but four states, 7, 8, 10 and 11.

The coupling constant in pyridine corresponding to J_{XY} was found to be $0{\cdot}4$ cps.[3] It can also be seen from the group of lines assigned to X and Y that J_{XY} should be small. It was therefore assumed that $J_{XY} = 0$ to carry out the analysis. The validity of this assumption can be judged from the extent to which the analysis on this basis accounts for the observed spectrum. Substituting $J_{XY} = 0$ the secular equation can be completely

TABLE II

*Calculated transition frequencies and relative intensities, and observed frequencies for α-picoline**

Sl. No.	Transition†	Calculated frequency (in cps.)	Observed frequency‡ (in cps.)	Calculated relative intensity
ABC lines				
1	2′→ 1	20·8	21·0	0·40
2	9′→ 5	18·8	18·9	0·41
3	7′→ 3′	16·8		0·14
4	14′→11′	14·4	15·3	0·37
5	8′→ 3′	14·3		0·46
6	7′→ 4′	13·2		0·71
7	13′→11′	11·8		0·49
8	14′→10′	11·7	12·0, 10·9	0·33
9	8′→ 4′	10·7		0·24
10	13′→10′	9·2		0·21
11	15→ 6′	6·7	6·3	2·02
12	16→12′	4·7	4·3	2·04
13	4′→ 1	1·1	..	0·66
14	6′→ 3′	− 0·6		2·58
15	10′→ 5	− 2·0	− 1·9,	0·20
16	3′→ 1	− 2·5	− 3·4§	2·16
17	12′→11′	− 3·6		2·82
18	6′→ 4′	− 4·2		0·69
19	11′→ 5	− 4·6		2·37

TABLE II (*Contd.*)

Sl. No.	Transition†	Calculated frequency (in cps.)	Observed frequency‡ (in cps.)	Calculated relative intensity
20	12′→10′	− 6·3	− 6·2	0·22
21	7′→ 2′	− 6·6		0·92
22	15 → 8′	− 8·2		0·30
23	8′→ 2′	− 9·0	− 8·0	0·48
24	14′→ 9′	− 9·1		1·21
25	15 → 7′	−10·7		0·71
26	16 →13′	−10·8	−10·5,	0·53
27	13′→ 9′	−11·6	−13·1,	0·83
28	16 →14′	−13·3	−14·8?	0·92
29	6′→ 2′	−23·9	..	0·0042
30	12′→ 9′	−27·1	..	0·0071
X lines				
1	9′→ 3′	24·0	..	0·0009
2	9′→ 4′	21·3	..	0·001
3	14′→ 6′	16·4	..	0·001
4	13′→ 6′	13·9	..	0·002
5	10′→ 3′	4·1	4·1	0·38
6	5 → 1	3·6		1·00
7	9′→ 2′	1·5	2·0,	0·99
8	14′→ 8′	1·5	0·5	0·71
9	11′→ 3′	1·5		0·60
10	10′→ 4′	0·5		0·49

TABLE II—(*Contd.*)

Sl. No.	Transition†	Calculated frequency (in cps.)	Observed frequency‡ (in cps.)	Calculated relative intensity
11	14′→ 7′	− 0·9	− 1·9	0·30
12	13′→ 8′	− 1·0		0·007
13	12′→ 6′	− 1·6		1·00
14	11′→ 4′	− 2·1		0·52
15	13′→ 7′	− 3·5	− 3·5§	0·98
16	16 →15	− 3·6		0·46
17	12′→ 8′	−16·5	..	0·0008
18	12′→ 7′	−18·9	..	0·0011
19	10′→ 2′	−19·2	..	0·0002
20	11′→ 2′	−21·9	..	0·0002

* The frequencies of ABC transitions are expressed relative to $\frac{1}{2}(\nu_A + \nu_B + \nu_C)$ as the origin while those of X transitions are expressed relative to ν_X as the origin.

† The states involved in the transitions are labelled just as in I.

‡ Average standard deviation for the observed frequency determinations is about ± 0·25 cps.

§ These lines are observed only as humps. The line at −14·8 cps. does not seem to fit in the analysis of the spectrum.

solved, and explicit expressions may be derived for all the transition energies and relative intensities.

The problem now becomes very much similar to that of 1-fluoro, 2, 4-dinitrobenzene (I). By replacing C and X by X and Y respectively and then substituting $J_{XY} = 0$ in Tables II (*a*), II (*b*) and II (*c*) of I[5] the transition energies and relative intensities involved in this problem are obtained.

In the present case only the AB part of the spectrum has been analyzed as the X and Y lines (at the lower field in the observed spectrum) are hardly resolved. The theoretical AB spectrum consists of four quartets as in the case of 1-fluoro, 2, 4-dinitrobenzene, and the assignment of the lines to these quartets has been done in a similar manner. From this assignment

the values of J_{AB}, $(\nu_A - \nu_B)$, $(J_{AX} - J_{BX})$ and $(J_{AY} - J_{BY})$ were obtained. The centres of D_+, F_+, F_- and D_- quartets (*see* I) in the AB spectrum, with reference to $\frac{1}{2}(\nu_A + \nu_B)$, are respectively given by

$$\left.\begin{aligned} &\tfrac{1}{4}[(J_{AX} + J_{BX}) + (J_{AY} + J_{BY})] \\ &\tfrac{1}{4}[-(J_{AX} + J_{BX}) + (J_{AY} + J_{BY})] \\ &\tfrac{1}{4}[(J_{AX} + J_{BX}) - (J_{AY} + J_{BY})] \\ &\tfrac{1}{4}[-(J_{AX} + J_{BX}) - (J_{AY} + J_{BY})] \end{aligned}\right\} \qquad (7)$$

and from these the values of $(J_{AX} + J_{BX})$ and $(J_{AY} + J_{BY})$ were obtained. Thus all the parameters except $(\nu_X - \nu_Y)$ were derived from the analysis of AB spectrum alone. It was, however, not possible to deduce the signs of the coupling constants from the analysis, as was done in the case of 1-fluoro, 2, 4-dinitrobenzene, since no information could be obtained from the X and Y lines. The analysis was therefore carried out assuming all the coupling constants to be positive. The values of the parameters finally obtained are as follows (in cycles per second):

$$\left.\begin{aligned} (\nu_A - \nu_B) &= 10{\cdot}3 \\ J_{AB} &= 7{\cdot}9 \\ J_{AX} &= 1{\cdot}7 \\ J_{BX} &= 4{\cdot}8 \\ J_{AY} &= 2{\cdot}5 \\ J_{BY} &= 1{\cdot}2 \\ J_{XY} &= 0 \end{aligned}\right\}. \qquad (8)$$

The error involved in any of these values is not more than $\pm 0{\cdot}4$ cps.

As all the lines of X and Y lie very close within a small region in the observed spectrum, $(\nu_X - \nu_Y)$ was taken as zero to calculate the spectrum.* The transition frequencies and relative intensities calculated on the basis of the parameters in equation (8) are given in Table III along with the observed frequencies. The calculated spectrum is shown in Fig. 3 (*b*). The good agreement between the observed and calculated spectra lends justification to the assumptions made in the analysis.

5. γ-PICOLINE

The general theory of A_2X_2 type of spectra was given earlier by several authors,[8–10] according to which the spectrum would consist of two groups

* When $(\nu_X - \nu_Y) = 0$ and $J_{XY} = 0$, the ABXY system may also be called as an ABXX' system.

TABLE III

Calculated transition frequencies and relative intensities, and observed frequencies for β-picoline

Transition No.*	Calculated frequency† (in cps.)	Observed frequency‡ (in cps.)	Calculated relative intensity
AB lines			
2	36·7	36·7	0·36
6	38·9	39·0	0·46
10	39·1		0·30
14	41·3	41·4§	0·42
1	44·6	44·7§	1·64
5	46·8	46·7§	1·54
9	47·0		1·70
3	49·1	49·1	1·64
13	49·2		1·58
11	50·5	50·3	1·70
7	53·6	53·7	1·54
15	54·9	54·9	1·58
4	57·0	57·0	0·36
12	58·4	58·3	0·30
8	61·5	61·5	0·46
16	62·8	62·8	0·42
X lines			
5	−13·6	..	0·0041
11	−12·5	..	0·0058
7	− 3·4	− 3·1π	1·0
12	− 3·4		1·0
2	− 1·2	− 0·9	0·9959
8	− 1·1		0·9942

TABLE III (*Contd.*)

Transition No.*	Calculated frequency† (in cps.)	Observed frequency‡ (in cps.)	Calculated relative intensity
9	1·1	1·0	0·9942
3	1·2		0·9959
6	3·4	3·0π	1·0
1	3·4		1·0
10	12·5	..	0·0058
4	13·6	..	0·0041
Y lines			
12	−14·2	..	0·0007
10	−11·9	..	0·0014
6	− 1·8	− 0·9	1·0
8	− 1·8		1·0
5	− 0·6		0·9993
4	− 0·5		0·9986
3	0·5	1·0	0·9986
7	0·6		0·9993
2	1·8		1·0
1	1·8		1·0
9	11·9	..	0·0014
11	14·2	..	0·0007

* The transition Nos. for the AB, X and Y spectra correspond to those in Tables II (*a*), II (*b*) and II (*c*) respectively. The expressions are to be modified in the present case by replacing C and X by X and Y respectively.

† The calculated frequencies are given with reference to $\nu_x (= \nu_y)$ as the origin.

‡ The observed frequencies are given with respect to the centre of the XY group of lines. Average standard deviation for the observed frequency determinations is about ± 0·2 cps.

§ The peaks corresponding to these lines are not clearly identified in the spectra.

π These lines are observed only as humps.

of lines each comprising of twelve transitions, and which are completely identical in positions and intensities with reference to their respective centres. In the observed spectrum the group of lines on the lower field consists of four lines, while the structure of the other group appears to be a little complicated probably due to the coupling of these protons with the methyl protons. However, a general resemblance between the two groups can be seen.

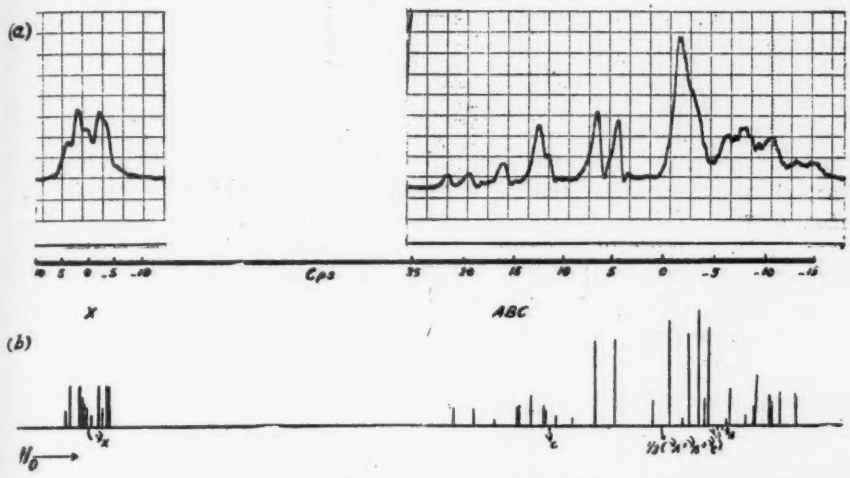


FIG. 3. H^1 NMR spectrum of β-picoline at 40 Mc./sec. (*a*) Experimental; (*b*) Calculated XY spectrum: 1 cm. = 6·368 cps. AB spectrum: 1 cm. = 4·221 cps.

As the coupling between the two protons *ortho* to nitrogen was observed to be very small in pyridine, 4-pyridine-d_1[3] and β-picoline (present work) it has been assumed to be equal to zero for the present analysis. The spectrum then belongs to the A_2X_2 class with K = M.* A typical half of such a spectrum consists of six transitions symmetrical with respect to the centre as given by Bernstein *et al.*[9, 10] The group of lines at the lower field in the observed spectrum consists of only four lines symmetrical with respect to the centre. The outer pair may be assigned to the transitions 1, 2 and 3, 4 and the inner pair to the transitions 6, 10 and 7, 11 (transition numbers as in Table 6–18 of reference 10). The other two lines (corresponding to the transitions 5, 9 and 8, 12) are comparatively weak and are

* The transition energies and intensities were conveniently expressed in terms of K, L, M and N defined as $K = J_A + J_X$, $L = J - J'$, $M = J_A - J_X$, $N = J + J'$ (Fig. 6). *See* also references 9 and 10.

expected to occur slightly outside the pair of lines at $\pm 3{\cdot}1$ cps. from the centre. As no absorption is indicated at these positions it was assumed

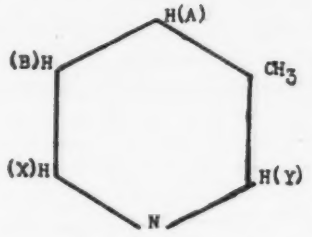


FIG. 4. β-picoline.

that these lines coincide with the strong lines at $\pm 3{\cdot}1$ cps. within experimental error. From the mutual separations in the observed spectrum we then get*

$$\left.\begin{aligned} N &= 6{\cdot}05 \text{ cps.} \\ K + \sqrt{K^2 + L^2} &= 6{\cdot}05 \text{ cps.} \\ \sqrt{K^2 + L^2} - K &= 2{\cdot}95 \text{ cps.} \end{aligned}\right\}. \tag{9}$$

From equation (9) the coupling constants were obtained as

$$\left.\begin{aligned} J &= 5{\cdot}1 \text{ cps.} & J_A &= 1{\cdot}6 \text{ cps.} \\ J' &= 0{\cdot}9 \text{ cps.} & J_X &= 0 \text{ cps.} \end{aligned}\right\}. \tag{10}$$

The error involved in any of these parameters is not more than $\pm 0{\cdot}4$ cps. The calculated spectrum is shown in Fig. 5 (*b*).

6. GENERAL COMMENTS

The coupling constants obtained from all these analyses do not differ in any striking manner from those in pyridine obtained by Schneider *et al.*[3] This is in line with the general observation that the spin coupling constants are not much sensitive to substitution. The chemical shift values also do not differ very much from the corresponding values in pyridine indicating that methyl substitution does not drastically alter the shielding of the ring protons in pyridine. The lines in all the three spectra are rather broad

* 6·05 represents an average of the mutual separations between the intense lines in the A_2 and X_2 spectra. 2·95 represents the separation between the two inner components in X_2 spectrum only as those in the A_2 multiplet are not easily identified.

presumably due to the impurities in the samples. The accuracy of the parameters is somewhat impaired due to this reason.

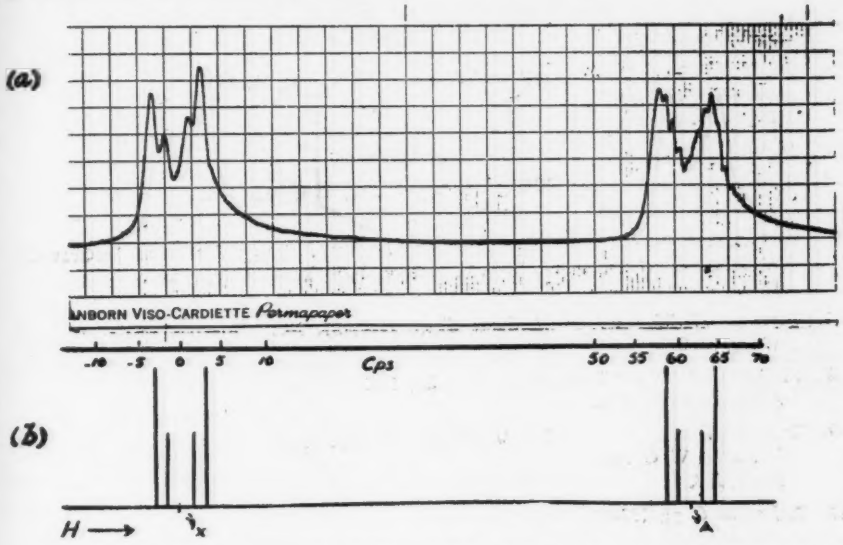


FIG. 5. H^1 NMR spectrum of γ-picoline at 40 Mc./sec. (*a*) Experimental; (*b*) Calculated. 1 cm. = 6·491 cps.

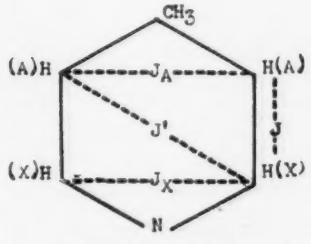


FIG. 6. γ-picoline.

ACKNOWLEDGEMENT

The authors wish to express their sincere thanks to Dr. H. Sripathi Rao, Central Fuel Research Institute, Jealgora, for providing them with the samples used in this work. Thanks are also due to the University Grants Commission for their support in developing the Microwave and Radio-frequency Laboratory at Aligarh, and to the Council of Scientific and Industrial Research for the grant of a research scheme.

REFERENCES

1. Baker, E. B. .. *J. Chem. Phys.*, 1955, **23**, 1981.
2. Bernstein, H. J. and Schneider, W. G. *Ibid.*, 1956, **24**, 469.
3. Schneider, W. G., Bernstein, H. J. and Pople, J. A. *Ann. N.Y. Acad. Sci.*, 1958, **70**, 806.
4. Sripathi Rao, H. .. (Private communication).
5. Nageswara Rao, B. D. and Venkateswarlu Putcha *Proc. Ind. Acad. Sci.*, 1960, **52**, 109.
6. Pople, J. A., Schneider, W. G. and Bernstein, H. J. *High Resolution Nuclear Magnetic Resonance*, McGraw-Hill Book Co., Inc., New York, 1959, p. 98.
7. Fessenden, R. W. and Waugh, J. S. *J. Chem. Phys.*, 1959, **31**, 996.
8. McConnell, H. W., McLean, A. D. and Reilly, C. A. *Ibid.*, 1955, **23**, 1152.
9. Bernstein, H. J., Schneider, W. G. and Pople, J. A. *Can. J. Chem.*, 1957, **35**, 1060.
10. Reference 6, pp. 138–51.

SEARCH FOR PHYSIOLOGICALLY ACTIVE COMPOUNDS

Part V. Synthesis of Nitro Coumarins

By N. V. Subba Rao, F.A.Sc. and V. Sundaramurthy

(*Chemistry Department, Osmania University*)

Received May 25, 1961

The synthesis of nitro-substituted coumarins has been undertaken as part of a general scheme of search for physiologically active compounds, in view of the fact that nitro-substituted compounds have a unique place in the attack against pathogenic micro-organisms.

The preparation of 6-nitro[1], 7-nitro[2] and 8-nitro[3] coumarins by the Perkin condensation has been reported in literature. By heating the corresponding nitro salicylaldehydes with sodium phenylacetate and acetic anhydride, the 6-nitro, 8-nitro and 6:8-dinitro-3-phenyl coumarins[4] were prepared. The condensation of 5-nitro salicylaldehyde with ethyl acetoacetate in the presence of alkali gives the 6-nitro-3-acetyl coumarin.[5] 7-nitro-4-hydroxy coumarin was prepared by Julia and Tchernoff[6] following Anschutz[7] procedure.

In the present work a number of nitro coumarins substituted with different groups in 3 and 4 positions have been prepared using the corresponding nitro-substituted salicylaldehydes and 3-nitro-2-hydroxy acetophenones.

Among the required intermediates, 3-nitro and 5-nitro salicylaldehydes have been prepared by the direct nitration of salicylaldehyde according to Diehl[8] and 6-nitro salicylaldehyde by the Reimer-Tiemann reaction on *m*-nitro phenol.[9] 4-Nitro salicylaldehyde is an abnormally substituted derivative and is difficult to prepare. This was originally synthesised by Segesser and Calvin[10] from 4-nitro-2-acetoxy toluene through photobromination and hydrolysis and later by Libermann following Thiele's oxidation procedure. In both the cases the yields were poor. The compound has now been prepared following the recent method of Goldberg and Walker[11] by the Khronke reaction on 4-nitro-2-acetoxy benzyl bromide.

The nitration of *o*-hydroxy acetophenone oxime was reported by Lindemann and Romanoff[12] whereby the 3- and 5-nitro isomers were obtained.

It was therefore considered worthwhile to investigate if the direct nitration of *o*-hydroxy acetophenone also gave the two isomers. When the nitration was carried out at 15° C. in acetic acid medium with fuming nitric acid, the bulk of the product formed was found to be the 3-nitro isomer reported by the other workers.

Starting from 6-nitro salicylaldehyde, 5-nitro coumarin was prepared by Perkin's reaction. Following Bargellini's procedure 5-nitro-3-phenyl and 7-nitro-3-phenyl coumarins could be prepared from 6-nitro and 4-nitro salicylaldehydes respectively. By the condensation of 6-nitro, 5-nitro and 3-nitro salicylaldehydes with ethyl acetoacetate the 5-nitro, 6-nitro and 8-nitro-3-acetyl coumarins respectively could be obtained. Condensation of 3-nitro-2-hydroxy acetophenone with sodium phenylacetate and acetic anhydride, cyanoacetic ester [13] and ethyl carbonate gave the 8-nitro-4-methyl-3-phenyl, 8-nitro-4-methyl-3-cyano and 8-nitro-4-hydroxy coumarins respectively.

In toxicity tests, the nitro-3-phenyl coumarins have been found to be active against bacteria and fungi of select species but are not appreciably toxic to fish.

EXPERIMENTAL

1. *5-nitro coumarin.*—6-Nitro salicylaldehyde[9] (0·2 g.), anhydrous sodium acetate (1 g.) and acetic anhydride (10 ml.) were refluxed at 170-80° C. for about four hours in a paraffin-bath. The reaction mixture was poured on crushed ice and the solid that separated was crystallised from glacial acetic acid in yellow needles (0·2 g.), m.p. 160° C. (Found: C, 56·9; H, 2·5; N, 6·9; $C_9H_5NO_4$ requires C, 56·5; H, 2·6; N, 7·3%).

2. *5-Nitro-3-phenyl coumarin.*—6-Nitro salicylaldehyde[9] (1 g.), sodium phenylacetate (2 g.) and acetic anhydride (15 ml.) were refluxed in an oil-bath at 170–80° C. for five hours and then poured in ice-cold water. After keeping overnight, the solid that separated was filtered, washed free from acid and recrystallised from glacial acetic acid, yellow needles (0·6 g.), m.p. 140° C. (Found: C, 67·5; H, 3·7; N, 5·3; $C_{15}H_9NO_4$ requires C, 67·4; H, 3·8; N, 5·2%).

3. *7-Nitro-3-phenyl coumarin.*—Starting from 4-nitro salicylaldehyde,[11] 7-nitro-3-phenyl coumarin was prepared following the procedure described in 2. The product (0·6 g.) obtained was recrystallised from glacial acetic acid, golden yellow needles, m.p. 242° C. (Found: C, 67·2; H, 3·8; N, 5·2; $C_{15}H_9NO_4$ requires C, 67·4; H, 3·8: N, 5·2%).

4. 8-*Nitro*-3-*acetyl coumarin*.—3-Nitro salicylaldehyde[8] (1 g.) was dissolved in ethyl acetoacetate (2 ml.) after the addition of a small quantity of alcohol and heating. The hot solution was cooled to about 40° C. and three to four drops of piperidine were added. The liquid became viscous, and on cooling and scratching solidified. The solid was triturated with a small quantity of alcohol and filtered. The residue was washed with cold alcohol until free from colour and recrystallised from alcohol-acetone mixture as pale yellow needles (0·6 g.), m.p. 200° C. (Found: C, 56·7; H, 3·2; N, 6·4; $C_{11}H_7NO_6$ requires C, 56·6; H, 3·0; N, 6·0%).

5. 6-*Nitro*-3-*acetyl coumarin*.—5-Nitro salicylaldehyde[8] (1 g.) was condensed with ethyl acetoacetate (2 ml.) following the procedure described in 4. The product (0·8 g.) obtained on recrystallisation from alcohol-acetone mixture gave pale yellow needles, m.p. 192° C. (Wahlburg,[5] m.p. 193° C.).

6. 5-*Nitro*-3-*acetyl coumarin*.—This substance was prepared from 6-nitro salicylaldehyde following the procedure described above and recrystallised from glacial acetic acid as light yellow needles, m.p. 156° C. (Found C, 56·7; H, 3·0; N, 5·9; $C_{11}H_7NO_6$ requires C, 56·6; H, 3·0; N, 6·0%).

7. 8-*Nitro*-4-*methyl*-3-*phenyl coumarin*.—3-Nitro-2-hydroxy acetophenone was prepared by the direct nitration of *o*-hydroxy acetophenone at 15–20° C., m.p. 87–88° C. (Lindemann and Romanoff,[12] m.p. 88° C.).

3-Nitro-2-hydroxy acetophenone (1 g.), sodium phenylacetate (2 g.), and acetic anhydride (25 ml.) were refluxed in an oil-bath at 170–80° C. for five hours and then poured on crushed ice. The pasty mass that separated on leaving overnight was treated with cold alcohol and the solid obtained was recrystallised from glacial acetic acid as pale yellow needles (0·8 g.), m.p. 228° C. (Found: C, 68·2; H, 4·4; N, 4·6; $C_{16}H_{11}NO_4$ requires C, 68·3; H. 3·9; N, 4·9%).

8. 8-*Nitro*-4-*methyl*-3-*cyano coumarin*.—A mixture of 3-nitro-2-hydroxy acetophenone (2 g.), ethyl cyanoacetate (2 g.) and sodium ethoxide (0·1 g. in 20 ml. of absolute alcohol) was refluxed for about two hours when crystals began to appear. The mixture was cooled, the crystals that separated were filtered and washed with small amounts of cold alcohol to remove the colour. On recrystallisation from acetone-water mixture pale yellow needles were obtained (0·5 g.), m.p. 219° C. (Found: C, 57·2; H, 3·0; N, 11·9; $C_{11}H_6N_2O_4$ requires C, 57·4; H, 2·6; N, 12·2%).

9. 8-*Nitro*-4-*hydroxy coumarin*.—3-Nitro-2-hydroxy acetophenone (1·5 g.) was mixed with ethyl carbonate (10 ml.) in the presence of sodium

powder (1·5 g.). After the initial vigorous reaction had subsided, the reaction mixture was heated on a steam-bath for one hour. Alcohol was then added to destroy the excess of sodium and the excess of ethyl carbonate was removed by ether extraction. The product obtained on acidification was recrystallised from ethyl alcohol as straw yellow needles, m.p. 118° C. (Found: C, 52·5; H, 2·3; N, 6·2; $C_9H_5NO_5$ requires C, 52·6; H, 2·4; N, 6·7%).

SUMMARY

5-Nitro, 5-nitro-3-phenyl, 7-nitro-3-phenyl, 5-nitro-3-acetyl, 6-nitro-3-acetyl, 8-nitro-3-acetyl, 8-nitro-4-methyl-3-phenyl, 8-nitro-4-methyl-3-cyano and 8-nitro-4-hydroxy coumarins have been prepared.

REFERENCES

1. Tagae .. *Ber.*, 1889, **20**, 2110.
2. Libermann, Desnoes and Hengl — *Compt. Rend*, 1951, **232**, 2027; *Chem Abstr.*, 1952, **46**, 1542.
3. Kinkellin .. *Ber.*, 1891, **22**, 1706.
4. Bertram, Lovet and Roberts — *J. Chem. Soc.*, 1925, 1975.
5. Wahlburg .. *Ber.*, 1932, **65 B**, 1857.
6. Julia and Tchernoff .. *Bull. Soc. Chim. Fr.*, 1952, 779.
7. Anschutz .. *Ann.*, 1909, **367**, 169, 196; *Ber.*, 1903, **36**, 465.
8. Hach, Liggett and Diehl .. *Iowa State Coll. J. Sci.*, 1947, **21**, 316; *Chem. Abstr.*, 1948, **42**, 1240.
9. Ashley, Perkin and Robinson — *J. Chem. Soc.*, 1930, 396.
10. Segesser and Calvin .. *J. Amer. Chem. Soc.*, 1941, **63**, 825.
11. Goldberg and Walker .. *J. Chem. Soc.*, 1954, 2540.
12. Lindemann and Romanoff — *J. Prakt. Chem.*, 1929, **122** (ii), 214.
13. Schroeder and Link .. *J. Am. Chem. Soc.*, 1953, **75**, 1886.

KINETIC STUDIES IN ESTER HYDROLYSIS

Part XII. The Alkaline Hydrolysis of Succinates in Mixed Solvents Study of Consecutive Reactions

By P. S. Radhakrishnamurti

(Contribution from the Department of Chemistry, Madras Christian College, Tambaram)

Received September 15, 1961

(Communicated by Prof. S. V. Anantakrishnan, F.A.SC.)

In Parts X and XI of this series we reported the results of hydrolytic studies on the esters of benzoic and cinnamic acids. It was considered worthwhile to extend the investigations to a study of succinates involving a consecutive reaction as very little work on dibasic acids has been reported. Diethyl and dibenzyl succinates have been chosen for the present study.

Experimental

The esters and the solvents were purified by standard methods. The physical constants of the compounds used are given below:

	Boiling point	Dipole moment
Diethyl succinate	217·7° C.	2·3
	Melting point	
Dibenzyl succinate ..	42·5° C.	3·42

Rate studies were made as in earlier parts excepting that all the saponification experiments were conducted at the constant ionic strength of 0·02 M. This was done essentially to rule out the probability of any medium effects due to changes in ionic strength that will occur as the di-acid ion is produced.

The treatment that has been followed for the evaluation of rate constants of both the steps is that of Frost.[1] The method for calculation based upon Frost's treatment involved the graphical evaluation of $1/k$ from different time ratios.

Knowing the numerical values of 'r', t and B_0, using the relation $\log r = \log B_0 + \log k_1 + \log t$, k_1 was calculated. From this k_2 was later calculated by division as we know $k_2/k_1 = k$.

DISCUSSION

The rate constants are presented in Table I.

TABLE I

Solvent composition percentage of organic solvent (v/v)	Temperature					
	30° C.		35° C.		40° C.	
	I step	II step	I step	II step	I step	II step
	Ester: Diethyl succinate					
50% Dioxan ..	·1516	·0251	·1970	·0331	·2544	·04330
60% Dioxan ..	·1140	·0232	·1491	·0312	·1950	·04120
70% Dioxan ..	·0935	·0333	·1240	·0301	·1631	·04036
50% Acetone ..	·1185	·01950	·1575	·02625	·2073	·03501
60% Acetone ..	·0956	·01890	·1280	·02560	·1696	·03431
70% Acetone ..	·0750	·01828	·1010	·02510	·1346	·03401
	Ester: Dibenzyl succinate					
50% Dioxan ..	·1900	·0313	·2440	·0410	·3100	·0532
60% Dioxan ..	·1590	·0303	·2060	·0420	·2640	·0522
70% Dioxan ..	·1220	·0291	·1598	·0389	·2070	·0573
50% Acetone ..	·1487	·0246	·1950	·0325	·2530	·0425
60% Acetone ..	·1158	·0230	·1529	·0308	·2002	·0408
70% Acetone ..	·0900	·0217	·1200	·0292	·1585	·0389

The results obtained indicate that rate constants of the first step are invariably more than those of the second. Also the ratio of k_1/k_2 exceeds 2 at all temperatures. This is quite understandable, as in the saponification of the half ester, we have to envisage a charged species.[2]

An observation from Table I also reveals that the change of the alcoholic component from ethyl to benzyl has resulted in an upward trend of the kinetic rate. One can bring in here the analogy of alkyl halide hydrolysis

where the greater reactivity of the benzyl halide compared to ethyl halide is attributed to the carbonium ion stabilisation of the allylic system in benzyl halides.[3] A similar situation can be expected in the present study also.

Ingold[4] arrived at an equation based on the externally propagated polar factors for a symmetrical dicarboxylic ester:

$$k_1/k_2 = 2\,e^{WN/JRT}$$

where

$$W = e^2/\epsilon r.$$

Hence

$$k_1/k_2 = 2e^{e^2N/\epsilon rJRT}.$$

This equation was used to calculate the effective distance between the two carbethoxy groups. Table II indicates the abnormal values obtained.

TABLE II

Ester	Per cent dioxan (*v*/*v*)	*r*	Temperature
Diethyl succinate ..	50%	19·32	
	60%	34·26	40° C.
	70%	..	
Dibenzyl succinate ..	50%	19·47	
	60%	31·08	40° C.
	70%	57·09	

One has to examine the limitations of the Ingold's generalisation in understanding the abnormal ratio k_1/k_2.

The kinetic energy terms in the equilibrium equation have been disregarded. Internal electron displacements due to the external field are not considered. Electrical theory based on the hypothesis of continuous dielectric meets with difficulties when the distances involved are of the same magnitude as the dimensions of the molecule of the dielectric. The dielectric

constant of the solute is smaller than that of the solvent medium. The equation fails to account for temperature and medium effects. It seems indeed clear that any treatment is an approximation. Svirbely *et al.*[5] also support our conclusion that Ingold's equation is only an approximation.

The Arrhenius parameter and other thermodynamic constants are presented in Table III.

TABLE III

Percentage of organic solvent (*v*/*v*)	E		H		$Log_{10}pZ$		S	
	I	II	I	II	I	II	I	II
Ester: Diethyl succinate								
50% Dioxan ..	9754	10280	9141·8	9667	6·1125	5·8098	36·4	32·03
60% Dioxan ..	10120	10820	9507·8	10208	6·351	6·1682	29·56	30·40
70% Dioxan ..	10490	11270	9877·8	10658	6·532	6·4096	28·72	29·00
50% Acetone ..	10540	11040	9927·8	10428	6·670	6·2481	28·01	30·04
60% Acetone ..	10810	11240	10198	10628	6·7742	6·379	27·62	29·43
70% Acetone ..	11020	11700	10408	11488	6·820	6·6987	27·41	27·96
Ester: Dibenzyl succinate								
50% Dioxan ..	9226	9997	8613·8	9385	5·930	5·7039	31·49	32·52
60% Dioxan ..	9557	10260	8944·8	9648	6·092	5·8782	30·74	31·72
70% Dioxan ..	9965	10700	9352·8	10087	6·272	6·1799	29·91	30·34
50% Acetone ..	10010	10300	9397·8	9688	6·372	5·8129	29·95	32·03
60% Acetone ..	10310	10810	9697·8	10198	6·4953	6·1456	28·89	30·45
70% Acetone ..	10680	10000	10068	10388	6·616	6·2674	28·34	29·94

For each stage of hydrolysis separately E and $log_{10}pZ$ tend to increase together. A plot of log E and $log_{10}pZ$ as well as a plot of $log_{10}pZ$ against 1/E give linear plots, as it should be on the basis of thermodynamic considerations if both the Arrhenius parameters control the reaction rate.

Comparing the first and second steps it is easily seen that the activation energy of the first step is slightly lower than that of the second step. $Log_{10}pZ$

shows a decreasing trend from the first to second step. Entropy of activation increases numerically from the first to the second step. Perhaps one could explain the slowness of the second step on the basis of all the factors. This is definitely clear from the fact that there is repulsion from the electrical negative field present in the initial state of the second saponification step and the attack by the hydroxyl ions is definitely inhibited. Hammett *et al.*[6] have reported a lowering of activation energy for the second step of hydrolysis of diethyl succinate. But they have made it clear that there can be differences in the energy of activation within experimental errors.[7]

Turning to solvent influences we notice the sharp difference between acetone and dioxan solutions. Where both solvents have been studied acetone-water solutions invariably show a larger activation energy.

The ratio of k_1/k_2 (Table IV) falls as we increase the percentage of organic solvent in both the esters.[8-9]

TABLE IV

k_1/k_2 ratios	Temperature: 40° C.	
Percentage of dioxan (*v*/*v*)	Ethyl succinate	Benzyl succinate
50%	5·875	5·828
60%	4·732	5·057
70%	4·042	4·036

The k_1/k_2 ratio of diethyl and dibenzyl succinate is the same within the limits of experimental error.

The reason for the constancy of the ratio in the two esters in which alcoholic component has been varied can be well understood, as '*r*' is the distance between the cationic centre in the carboxylate ion of the ionic ester and mean focus of the reaction with the hydroxide ion in the carboxylic ester group. Since focus the hydroxide ion must attack the unsaturated carbonyl linking and not the saturated ether linking in the ester group it is to be expected that '*r*' could be, to a first approximation, independent of the nature of alocholic component, as what is observed in these hydrolytic studies is acyl oxygen fission.

SUMMARY

In continuation of our studies on ester hydrolysis, the kinetics of alkaline hydrolysis of succinates are reported. The rate constants of the first and second step of hydrolysis have been evaluated. A comparative study of the structural and solvent influences on the succinates is made.

ACKNOWLEDGEMENT

The author expresses his gratitude to Professor S. V. Anantakrishnan, F.A.SC., for suggesting the problem and supervising the work.

REFERENCES

1. Frost and Schwemer .. *J. Amer. Chem. Soc.*, 1952, **74**, 1268.
2. Meyer .. *Z. Physik. Chem.*, 1909, **67**, 257.
3. Branch and Calvin .. *Theory of Organic Chemistry*, Prentice Hall, New York, 1946.
4. Ingold .. *J. Chem. Soc.*, 1930, 1032.
5. Svirbely .. *J. Amer. Chem. Soc.*, 1959, **81**, 255.
6. Hammett .. *Ibid.*, 1958, **80**, 2415.
7. ———— .. Private Communication.
8. Ritchie .. *J. Chem. Soc.*, 1931, 3112.
9. Westheimer .. *J. Chem. Phys.*, 1942, **10**, 478.

HIGH RESOLUTION NMR SPECTRA OF SOME TRI-SUBSTITUTED BENZENES

By S. S. Dharmatti, F.A.Sc., G. Govil, C. R. Kanekar, C. L. Khetrapal and Y. P. Virmani

(Tata Institute of Fundamental Research and Atomic Energy Establishment, Trombay, Bombay-5)

Received October 6, 1961

Abstract

This paper presents the analysis of the proton magnetic resonance spectra of 2:4 dinitro phenol, 1-chloro 2:4 dinitro benzene, 1-nitro, 2-methyl, 3-chloro benzene (2-chloro, 6-nitro toluene) and 5-sulpho, 3-nitro benzoic acid based on the exact solution obtained by Jha for the splitting of NMR lines of a three nuclei system of the ABC type.

Introduction

The analysis of the high resolution proton magnetic resonance spectra of the ABC type has aroused great interest during recent times. Fessenden and Waugh (1959) have given several rules which allow one to reduce the total number of independent parameters in such a system by inspection of the observed spectrum. Alexander (1960), Richards and co-worker (1960) and Sheppard *et al.* (1960) have analysed the spectra of styrene and vinyl compounds, all of which belong to the ABC type. However, in all such cases the 3×3 matrices involved in the analysis were not solved in terms of explicit expressions but numerical computations were made to diagonalise these matrices. Recently Jha (1961) has solved these matrices and obtained explicit expressions for the intensities and the frequencies arising out of the fifteen allowed transitions in such a system.

In the present paper we report the analysis of some tri-substituted benzenes based on these expressions. In all these cases a guess of different parameters was first made to the first order of approximation. A good fit between the observed and the calculated spectra was then obtained by a few trial and error calculations using Jha's expressions.

Experimental

(1) *NMR Measurements*

The spectra were recorded on a Varian High Resolution NMR Spectrometer operating at 60 Mc./s. The distances between the various peaks were

measured by the usual side band technique correct to $\pm$ 0·3 c./s. and have been expressed in frequencies relative to ν_0, the mean Larmor frequency for the three phenyl protons forming the ABC system. The intensities were measured in terms of amplitudes of the various peaks. It may be pointed out that this procedure of measuring intensities may create an error of about $\pm$ 15% which is rather large but inevitable in the absence of an elaborate integrating system; however, the procedure was satisfactory in most cases except when comparison was to be made between the observed and the calculated intensities of peaks which were not very well resolved. In such cases the observed intensities of the peaks which were in between two peaks were found to be always higher. The resolution under which these spectra were recorded was about 0·3 c./s. at the operating frequency of 60 Mc./s.

(2) *Chemicals*

(*a*) The sample of 2-chloro, 6-nitrotoluene was Eastman Kodak's and the spectrum was taken in solution in BDH 'Analar' grade carbon tetrachloride.

(*b*) α-dinitro phenol (2:4 dinitrophenol) was obtained from E. Merck and its soluton in E. Merck tetra hydro-furan was used for observing the spectrum.

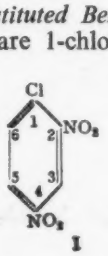
(*c*) 1-chloro, 2:4-dinitro benzene was prepared in the laboratory by nitration of chlorobenzene (Hoffman and Dame, 1919) and its solution in BDH 'Analar' grade carbon tetra chloride was used.

(*d*) The sodium hydrogen salt of 5-sulpho, 3-nitro benzoic acid was prepared by sulphonating benzoic acid followed by nitration according to the conditions given in the literature (Shah and Bhatt, 1933). The salt was then isolated by pouring the reaction mixture in saturated brine and was finally crystallised from water. The spectrum was taken in aqueous solution.

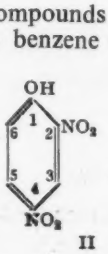
In all these cases sufficient nitrogen was bubbled through the solutions to remove any dissolved oxygen before recording the spectrum.

ANALYSIS OF THE SPECTRA

1, 2, 4 *Tri-substituted Benzenes.*—The compounds of this type which have been studied are 1-chloro, 2:4-dinitro benzene (I) and 2:4-dinitro phenol (II).



I



II

Because of the low *para* coupling constant (J_{36}) which in general has been reported to be less than 0·5 c./s. (Pople, Bernstein, Schneider, 1959) the spectrum of this type is comparatively simple to analyse. For these compounds one expects a spectrum which generally consists of a doublet due to 3 position proton the separation of which will give J_{35} to the first order of approximation, a doublet due to 6 position proton the separation of which will give J_{56} to the first order and a quartet due to 5 position proton. Since the *ortho* and *meta* coupling constants (J_{56} and J_{35}) involved are widely different in magnitude (Pople, Bernstein, Schneider, 1959) one can analyse the spectrum without ambiguity.

The proton resonance spectra of the compounds (I) and (II) are shown in Figs. 1 and 2. It is seen from the spectrum that the coupling constant

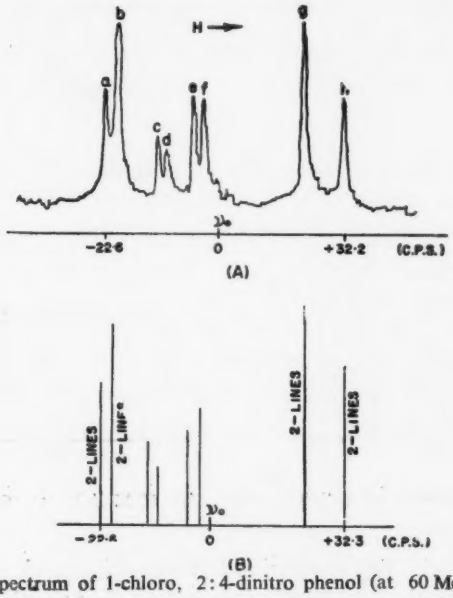


FIG. 1. NMR spectrum of 1-chloro, 2:4-dinitro phenol (at 60 Mc./s.). A. Observed; B. Calculated.

J_{36} must be less than 0·3 c./s. (the order of resolution in our experiment) since no further splitting of doublets for proton in 3 and 6 positions is observed. These considerations lead to an assignment to the various lines in the observed spectra of 1-chloro, 2:4-dinitro benzene and α-dinitro phenol. Thus lines (*a*) and (*b*) are due to proton in position (3) and (*g*) and (*h*) due to the proton in position 6. The proton in position (5) gives rise to a quartet represented

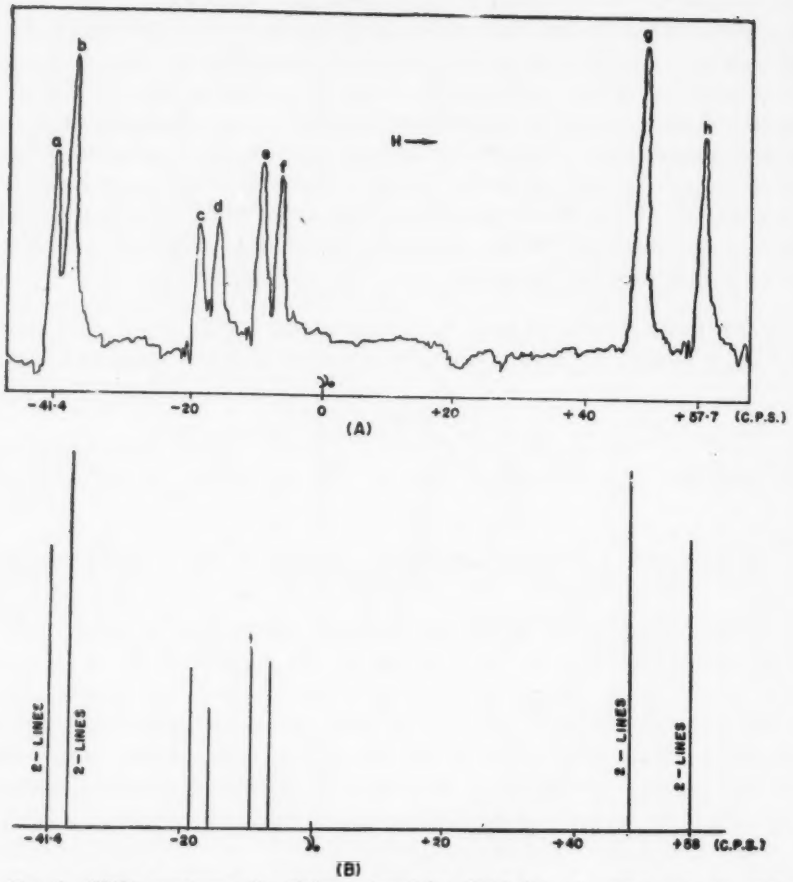


FIG. 2. NMR spectrum of α-dinitro phenol (at 60 Mc./s.). A. Observed; B. Calculated.

by lines *c*, *d*, *e* and *f*. The separation between (*a*) and (*b*) gives J_{35} and that between (*g*) and (*h*) gives J_{56} to the first orders of approximations.

Using Jha's expressions, the following values have been assigned to the various parameters:—

1-*chloro*, 2:4-*dinitrobenzene*

$$\nu_3 = -21{\cdot}3 \pm 0{\cdot}2 \text{ c./s.} = -0{\cdot}355 \pm 0{\cdot}003 \text{ p.p.m.}$$

$$\nu_5 = -6{\cdot}4 \pm 0{\cdot}2 \text{ c./s.} = -0{\cdot}107 \pm 0{\cdot}003 \text{ p.p.m.}$$

$\nu_6 = +27{\cdot}7 \pm 0{\cdot}2$ c./s. $= +0{\cdot}462 \pm 0{\cdot}003$ p.p.m.

$J_{35} = 2{\cdot}7 \pm 0{\cdot}2$ c./s.

$J_{56} = 8{\cdot}7 \pm 0{\cdot}2$ c./s.

$J_{36} < 0{\cdot}3$ c./s.

2: 4-*dinitro phenol*

$\nu_3 = -39{\cdot}9 \pm 0{\cdot}1$ c./s. $= -0{\cdot}665 \pm 0{\cdot}002$ p.p.m.

$\nu_5 = -13{\cdot}1 \pm 0{\cdot}1$ c./s. $= -0{\cdot}218 \pm 0{\cdot}002$ p.p.m.

$\nu_6 = +53{\cdot}1 \pm 0{\cdot}1$ c./s. $= +0{\cdot}885 \pm 0{\cdot}002$ p.p.m.

$J_{35} = 2{\cdot}9 \pm 0{\cdot}1$ c./s.

$J_{56} = 9{\cdot}2 \pm 0{\cdot}2$ c./s.

$J_{36} < 0{\cdot}3$ c./s.

The theoretical spectra constructed on the basis of these values have also been shown for each of the two compounds in Figs. 1 and 2 for comparison.

In both these compounds the proton in position 3 has the least resonance frequency. This result is expected in view of the presence of the two nitro-groups having electron withdrawing power and thus decreasing the electron density at the 3 position.

1, 2, 3 (1, 2, 6) *tri-substituted benzenes*

Among the various 1, 2, 3 tri-substituted benzenes only one compound, namely, 1-nitro, 2-methyl, 3-chloro benzene (III) was studied as an example of ABC system.

III

For this compound the spectrum should consist of four lines due to each of the protons 4, 5 and 6 and three lines due to their combinations according to the general theory. The spectra obtained for this compound at 60 Mc./s. as well as at 30 Mc./s. are shown in Fig. 3. The intensities and the line separations in the two spectra indicate a strong coupling of the ABC protons.

Of the three substituents present in the molecule, the NO_2 group has the greatest electron withdrawal power and hence ν_6 is expected to be the least, ν_5 the highest and ν_4 should have an intermediate value. From the spectrum obtained at 60 Mc./s. lines *a*, *b*, *d* and *e* were therefore attributed to the transitions corresponding to the proton in the 6 positions; the separations between

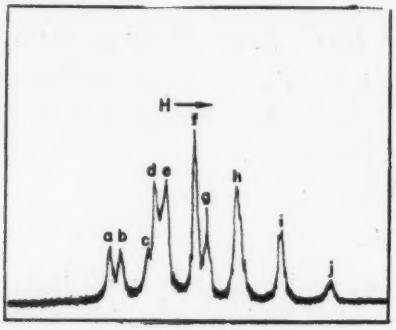


FIG. 3 A. NMR spectrum of 2-chloro, 6-nitro toluene (at 60 Mc./s.).

FIG. 3 B. NMR spectrum of 2-chloro, 6-nitro toluene (at 30 Mc./s.).

these lines give the first order values of J_{56} (*ortho*) and J_{46} (*meta*) in this compound. They are 8·4 c./s. and 2·9 c./s. respectively, in agreement with the generally expected values of these coupling constants. Similarly, lines *c*, *e*, *f* and *g* have been assigned to transitions corresponding to proton 4 and the lines *h*, *i*, *j* to those due to proton 5. The first order values of ν_4 and ν_5 and the various coupling constants thus obtained from the spectrum were then used in Jha's expressions for trial and error calculations. For a good agreement between the observed and the calculated spectra the following values had to be assigned to various parameters:

$\nu_6 = -0{\cdot}163 \pm 0{\cdot}003$ p.p.m.

$\nu_4 = -0{\cdot}047 \pm 0{\cdot}003$ p.p.m.

$\nu_5 = +0{\cdot}217 \pm 0{\cdot}003$ p.p.m.

$J_{46} = 2{\cdot}3 \pm 0{\cdot}2$ c./s.

$J_{45} = 8{\cdot}0 \pm 0{\cdot}2$ c./s.

$J_{56} = 8{\cdot}0 \pm 0{\cdot}2$ c./s.

The spectrum (Fig. 3 B) at 30 Mc./s. obtained incidentally in an earlier experiment also gave assignments in good agreement with the above values. Table I shows at a glance the general agreement between the calculated and the observed values of the frequencies and the intensities of the allowed transitions in this compound at 60 Mc./s. as well as at 30 Mc./s.

1, 3, 5 *Tri-substituted Benzenes*

The proton resonance spectra of 1, 3, 5 tri-substituted benzenes are in general more difficult to analyse than the previous cases. All the coupling constants for such compounds are of the same order $J_{meta} \approx 1$ to 3 c./s. and thus the two middle lines in each group A, B, C will in general not be resolved and, therefore, the spectrum will consist of nine lines. One can get the values of the three coupling constants and the two chemical shifts from the analysis but the assignment of these values to the three protons in the system has to be properly reasoned out.

As an example of 1, 3, 5 tri-substituted benzenes, we have studied the proton resonance in a saturated aqueous solution of sodium hydrogen salt of 5-sulpho, 3-nitro benzoic acid (IV).

IV

The total spectrum (Fig. 4) of the ABC type protons covers a narrow range of 11·5 c./s. in this case. Using Jha's expressions, it was found that the following parameters gave the best agreement between the theoretical and the observed spectra.

$\nu_A = -3{\cdot}8 \pm 0{\cdot}2$ c./s. $= -0{\cdot}063 \pm 0{\cdot}003$ p.p.m.

$\nu_B = -0{\cdot}5 \pm 0{\cdot}2$ c./s. $= -0{\cdot}008 \pm 0{\cdot}003$ p.p.m.

$\nu_C = +4{\cdot}2 \pm 0{\cdot}2$ c./s. $= +0{\cdot}070 \pm 0{\cdot}003$ p.p.m.

$J_{AB} = 2{\cdot}2 \pm 0{\cdot}2$ c./s.

$J_{AC} = 1{\cdot}4 \pm 0{\cdot}2$ c./s.

$J_{BC} = 1{\cdot}5 \pm 0{\cdot}2$ c./s.

TABLE I

Calculated and observed spectra of 2-chloro, 6-nitro toluene

No.	30 Mc./s. spectrum				No.	60 Mc./s. spectrum			
	Frequencies		Relative intensities			Frequencies		Relative intensities	
	Obs. c./s.	Cal. c./s.	Obs.	Cal.		Obs. c./s.	Cal. c./s.	Obs.	Cal.
1	..	−18·4	0	0·00	1	..	−35·2	0	0·00
2	−11·3	−11·7	0·16	0·12	2	−22·2	−22·2	0·33	0·25
3	..	− 8·5	..	0·02	3	−19·3	−19·3	0·33	0·49
4	− 7·4	− 7·9	0·13	0·13	4	−15·7	−15·6	0·20	0·31
5	Unresolved	− 5·5	0·40	0·10	5	−15·1	−15·1	0·60	0·31
6	− 5·4	− 4·7		0·24	6	−12·7	−12·7	0·83	0·61
7	− 1·8	− 1·7	0·90	0·76	7	−12·1	−12·2	0·79	0·82
8	0·4	− 0·2	1·00	1·00	8	− 7·4	− 7·4	1·00	1·00
9	2·1	1·9	0·95	0·78	9	− 4·3	− 5·0	0·46	0·31
10	Unresolved	3·6	..	0·13	10	..	0·2	..	0·23
11	4·0	4·9	0·20	0·15	11	0·7	0·7	0·74	0·87
12	8·2	7·1	0·17	0·16	12	7·5	7·3	0·46	0·41
13	11·0	10·3	0·05	0·05	13	..	8·4	..	0·04
14	13·0	13·5	0·04	0·03	14	16·9	16·9	0·18	0·16
15	15·6	16·4	0·07	0·06	15	..	15·0	0	0·01

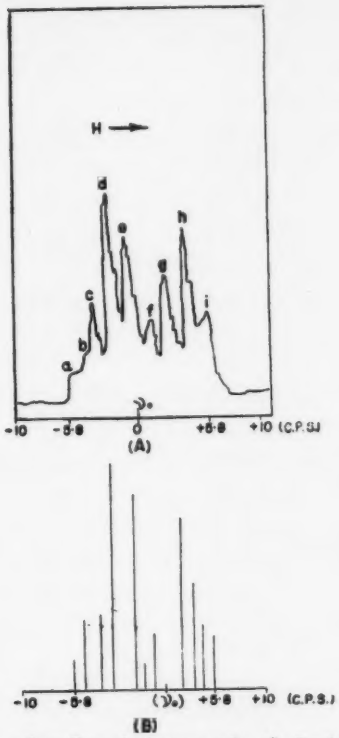


FIG. 4. NMR spectrum of sodium hydrogen salt of 5-sulpho, 3-nitro benzoic acid (at 60 Mc./s.). (A) Observed; (B) Calculated.

But the real difficulty in this case lies in determining which one of these shifts belongs to which proton. It seems reasonably right to presume that the shift ν_C is due to proton in position 6 because the $-NO_2$ group is the most electron withdrawing as compared with $-NaSO_3$ and —COOH groups and consequently the protons in 2 and 4 positions are expected to resonate at lower fields compared to this proton. It is difficult, however, to assign the frequency ν_B or ν_A to a particular proton in the remaining two, unless isotopic substitution method is employed.

From the values of the spin coupling constants derived from the analysis of the four compounds studied in this investigation, the following general observations can be made:

(1) The order of the magnitude of coupling constants is:

$$J_{ortho} > J_{meta} > J_{para}$$

(2) The values of the *ortho* coupling constants are in the range 8–9 c./s. the *meta* coupling constants vary from 1·0 to 3·0 c./s. and the *para* coupling constants are less than 0·3 c./s. These are the ranges so far observed for substituted benzenes (Pople *et al.*, 1959).

(3) Two of the *meta* coupling constants (J_{AC} and J_{BC}) in 5-sulpho, 3-nitro benzoic acid are very much lower than the normal values (Pople, Bernstein and Schneider, 1959). It appears that these low values are due to steric effects of the groups —COOH and —$NaSO_3$ from the work that is in progress in our laboratory, the details of which will be published elsewhere.

(4) All the observed coupling constants in this work have the same sign.

SUMMARY

It is thus found that the explicit expressions for the exact solution of the splitting up of NMR lines for the three nuclei of the type ABC are extremely useful for the analysis of the NMR spectra of the three spin systems.

REFERENCES

1. Alexander, S. .. *J. Chem. Phys.*, 1960, **32,** 1700.
2. Banwell, C. M. and Sheppard, N. *Mol. Phys.*, 1960, **3,** 351.
3. Bishop, E. O. and Richard, R. E. *Ibid.*, 1960, **3,** 114.
4. Fessenden, R. W. and Waugh, J. S. *J. Chem. Phys.*, 1959, **31,** 996.
5. Hoffman, E. J. and Dame, A. P. *J. Am. Chem. Soc.*, 1919, **41,** 1015.
6. Jha, S. S. .. *Proc. Ind. Acad. Sci.*, 1961, **54 A,** 13.
7. Pople, J. A., Schneider, W. G. and Bernstein, H. J. *High Resolution Nuclear Magnetic Resonance*, McGraw-Hill Publication, 1959, p. 193.
8. Shah, M. S. and Bhatt, C. T. *J. Chem. Soc.*, 1933, Part II, 1373.

GRAVIMETRIC DETERMINATION OF URANIUM AND THORIUM WITH 1-HYDROXY-XANTHONE

By Brahm Dev and B. D. Jain

(*Department of Chemistry, University of Delhi, Delhi-6*)

Received August 19, 1961

(Communicated by Dr. T. R. Seshadri, F.A.SC.)

It has been found that 1-hydroxy-xanthone can be used for the gravimetric determination of uranium and thorium in presence of large amounts of cerium (III) and lanthanum. The presence of cerium (IV) ions, even in minute quantities, interferes with the above determination, and if present, have to be reduced to cerous state.

When an alcoholic solution of 1-hydroxy xanthone is added to uranium (VI) salt solution, a deep orange-yellow complex is formed which on dilution with water gives a yellow precipitate yielding U_3O_8 on ignition. Uranium can thus be conveniently determined between pH 5 and 7 in quantities as low as 5·7 mg. Similarly an alcoholic solution of the reagent with thorium salt gives a deep yellow complex, which on dilution with water gives a yellow precipitate yielding thorium dioxide on ignition. Thorium can be determined between pH 4 and 4·5. As the reagent does not form any complexes with cerium (III) and lanthanum, the determinations of uranium and thorium can be accurately achieved in presence of large excess of cerium (III) or lanthanum. During the estimation of uranium and thorium or their separation from the above elements, sulphate ions should be absent since complex formation is totally inhibited by them. The presence of chloride and nitrate ions does not interfere.

Experimental

1-hydroxy-xanthone was prepared using the method followed by Desai *et al.*,[1] by condensing resorcinol with salicylic acid.

All metallic salts used were of A.R. (B.D.H.) quality.

The pH measurements were made with a Beckmann pH Meter using a suitable glass electrode.

Determination of uranium with 1-hydroxy-xanthone.—To about 50 ml. of an aqueous uranyl nitrate solution at suitable pH containing approximately

20 mg. of U_3O_8 and 2–3 gm. of ammonium nitrate, 25 ml. of alcohol and 10 ml. of 1% ethanolic solution of 1-hydroxy-xanthone were slowly added with constant stirring. The resulting deep orange-yellow complex was heated on a water-bath to completely remove the alcohol. On cooling and after the addition of water (100 ml.), the uranyl complex, along with the excess of the reagent, got precipitated. The flocculent precipitate after being allowed to settle for about ten minutes in the cold was filtered through Whatman filter-paper No. 40, washed with water, dried and ignited to U_3O_8. The results obtained are as accurate as obtained with oxine. Studies on the effect of pH on the formation of the uranyl complex show that the precipitation of uranium is quantitative between pH 5 and 7.

Determination of uranium in presence of cerium (III) and lanthanum.—Since the reagent does not form any complex with cerium (III) and lanthanum at pH 5–7 the procedure for the determination of uranium in their presence is the same as for the determination of uranium alone. The precipitate of the uranyl complex was thoroughly washed with water before final ignition. It has been found that uranium salts can be separated from large amounts of cerium (III) and lanthanum, as seen from Table I.

TABLE I

Determination of uranium in presence of cerium (III) and lanthanum

Weight of U_3O_8 taken = 22·8 mg.

Weight of CeO_2 added (mg.)	Weight of La_2O_3 added (mg.)	Weight of U_3O_8 found (mg.)
23·2	19·9	22·8
34·8	29·8	22·8
46·4	39·8	22·8
58·0	49·7	22·8
116·0	99·5	22·8
232·0	199·0	22·8

Determination of thorium.—To about 100 ml. aqueous thorium nitrate at pH 4–4·5 containing approximately 40 mg. of thorium dioxide and 2–3 gm,

of ammonium nitrate, 50 ml. of alcohol followed by 20 ml. of 1% ethanolic solution of 1-hydroxy-xanthone was added slowly with constant stirring. The deep yellow solution obtained was heated on a water-bath to remove the alcohol completely. On cooling and after the addition of water (100 ml.) the thorium complex along with the excess of the reagent got precipitated. The flocculent precipitate after being allowed to settle for about 10 minutes in the cold was filtered, washed with water, dried and ignited to ThO_2. The results obtained are as accurate as obtained with oxine. Studies on the effect of pH on the formation of the thorium complex show that the precipitation of thorium is complete at pH 4–4·5.

Determination of thorium in presence of cerium (III) and lanthanum.—The procedure for the determination of thorium in the presence of cerium (III) and lanthanum was the same as for the determination of thorium alone. The precipitated thorium complex was thoroughly washed with water before final ignition. It has been found that thorium salts can be separated from ten times its weight of cerium (III) and lanthanum as seen from Table II.

TABLE II

Determination of thorium in presence of cerium (III) and lanthanum

Weight of ThO_2 taken = 20·6 mg.

Weight of CeO_2 added (mg.)	Weight of La_2O_3 found (mg.)	Weight of ThO_2 found (mg.)
23·2	19·9	20·6
34·8	29·8	20·6
46·4	39·8	20·6
58·0	49·7	20·6
116·0	99·5	20·6
232·0	199·0	20·6

DISCUSSION

Though the gravimetric determination of both uranium and thorium can be done, it is not possible to separate one from the other employing

1-hydroxy-xanthone, whereas with 1-hydroxy-3-methoxy xanthone, Saxena and Seshadri[2] found that uranium could be separated from thorium, as uranium was found not to precipitate below pH 5·0 and the optimum pH range for the precipitation of thorium was 2·6-4·5. When 1-hydroxy-xanthone is used, thorium is quantitatively precipitated between pH 4·0 and 4·5 and though the precipitation of uranium is quantitative only between pH 5·0 and 7·0 incomplete precipitation of uranium takes place below pH 5·0.

The present study shows that cerium (IV) interferes in the determination of both uranium and thorium when 1-hydroxy-xanthone is employed, whereas with 1-hydroxy-3-methoxy xanthone, it has been possible to determine uranium and thorium in presence of cerium (IV).[2] Both 1-hydroxy-xanthone and 1-hydroxy-3-methoxy xanthone have the same chelating groups and in both the cases 6-membered rings are formed.

The preparation of 1-hydroxy-xanthone involves the condensation of resorcinol with salicylic acid, while in case of 1-hydroxy-3-methoxy xanthone, phloroglucinol dimethyl ether is condensed with salicylic acid in presence of a condensing agent.[3] The convenient method of preparation of 1-hydroxy-xanthone gives it an advantage over 1-hydroxy-3-methoxy xanthone, as an analytical reagent, in spite of its other limitations.

ACKNOWLEDGEMENT

The authors are indebted to Prof. T. R. Seshadri, F.R.S., Head of the Department, for his keen interest and helpful discussions during the course of the above investigation.

SUMMARY

The gravimetric determination of uranium and thorium alone, as well as in the presence of about ten times the amount of cerium (III) and lanthanum, can be readily carried out by using 1-hydroxy-xanthone as complexing agent.

REFERENCES

1. Desai, B. M., Desai, (Miss) P. R. and Desai, R. D. — *J. Indian Chem. Soc.*, 1960, **37**, 53.
2. Saxena, G. M. and Seshadri, T. R. — *Proc. Ind. Acad. Sci.*, 1958, **47 A**, 238.
3. Mittal, O. P. and Seshadri, T. R. — *J. Sci. Ind. Res.* (*India*), 1955, **14 B**, 76.

CONSTITUTION OF RUVOSIDE

By S. Rangaswami, F.A.Sc. and E. Venkata Rao

(Department of Pharmacy, Andhra University, Waltair)

Received September 19, 1961

The isolation of two new crystalline glycosides designated as peruvoside and ruvoside from the fermented seed kernels of *Thevetia neriifolia* Juss. (Fam. Apocynaceæ) was announced by the authors[1] in a preliminary communication in 1958 wherein they also mentioned the isolation of L-thevetose as a product of hydrolysis of both peruvoside and ruvoside. In a subsequent brief note[2] they adduced evidence for the presence of an aldehydic group in peruvoside and reported the formation of ruvoside on reducing peruvoside with aluminium-amalgam.

In the course of a detailed study of the chemistry of thevetin B and thevetin A obtained by the fractionation of crude thevetin from the seeds of *Thevetia neriifolia*,[3] Bloch *et al.*[4] found that thevetin B is identical with cerberoside obtained by Chen and Steldt[5] from the seed kernels of *Cerbera odollam* Gaertn. (Fam. Apocynaceæ) and is represented by the structure previously assigned by Helfenberger and Reichstein[6] to thevetin in 1948, *viz.*, digitoxigenin-L-thevetose-D-glucose-D-glucose. Thevetin A was also found to be a trioside which undergoes hydrolysis with enzymes to give D-glucose and a monoside which was identified with peruvoside of Rangaswami and Rao.[1] Reduction of the aldehyde group in peruvoside to methyl *via* the cyclic thioketal gave neriifolin (II), thus giving for peruvoside the structure α-L-thevetoside of cannogenin[7] (= 19-oxo-neriifolin) (I). It followed that thevetin A resembles thevetin B in all respects except that C_{19} exists as a methyl group in thevetin B and as an aldehyde in thevetin A.

The constitution of peruvoside having been thus settled, that of ruvoside easily follows. The reduction of peruvoside to ruvoside previously brought about by means of aluminium-amalgam has now been confirmed using sodium borohydride as the reagent. Hence the constitution of ruvoside is 19-hydroxy-neriifolin (= α-L-thevetoside of cannogenol[7]) (III).

Experimental

Besides the experiments leading to the conversion of peruvoside to ruvoside, other experiments pertinent to the constitution of peruvoside and

ruvoside which have only been mentioned in the form of preliminary notes[1,2] and which have not been described anywhere in the literature till now are also briefly described below.

Peruvoside (*I*).—Colourless prisms from methanol or methanol-ether m.p. 160–64°/210–16°. Legal reaction: positive; Keller-Kiliani reaction: negative; colour with conc. sulphuric acid: yellow-deep yellow-pale brown. $[\alpha]_D^{30} = -69{\cdot}6° \pm 3°$ ($c = 1{\cdot}124$ in methanol). Found: C, 65·2; H, 8·4; $-OCH_3$, 5·9%. $C_{30}H_{44}O_9$ (I) requires: C, 65·7; H, 8·1; $-OCH_3$ (1), 5·7%.

Isoperuvoside.—This was obtained by the action of potassium hydroxide in methyl alcohol employing the conditions of (*a*) Smith[8] and (*b*) Sigg *et al.*[9] It crystallized from methanol as colourless needles, m.p. 228–30°. Legal reaction: negative. $[\alpha]_D^{32} = -76{\cdot}1° \pm 2°$ ($c = 0{\cdot}812$ in methanol). Found: C, 64·7; H, 8·4; $-OCH_3$, 5·8%. $C_{30}H_{44}O_9$ requires: C, 65·7; H, 8·1; $-OCH_3$ (1) 5·7%.

Isoperuvoside acetate.—This was prepared by the action of acetic anhydride and pyridine on isoperuvoside in the cold. It crystallized from acetone-ether as colourless needles, m.p. 235–38° (decomp). $[\alpha]_D^{31} = -36{\cdot}5° \pm 3°$ ($c = 0{\cdot}602$ in methanol). Found: C, 63·5; H, 7.7; $-OCH_3$, 5·2; $-COCH_3$, 12·9%. $C_{34}H_{48}O_{11}$ requires: C, 64·5; H, 7·6; $-OCH_3$ (1), 4·9; $-COCH_3$ (2), 13·6%.

Peruvoside semicarbazone prepared by the action of semicarbazide hydrochloride and sodium acetate in methyl acohol in the cold crystallized from dilute alcohol as colourless needles, m.p. 266–68° (decomp). Found: N, 7·1%. $C_{31}H_{47}O_9N_3$ requires: N, 6·9%.

Betaine hydrazone of peruvoside using Girard reagent T.—This was prepared by treating peruvoside (100 mg.) with Girard reagent T (freshly crystallized from absolute alcohol) (62 mg.) in methanol (10 ml.) and pure acetic acid (0·5 ml.). The product was worked up as per the procedure of Schindler and Reichstein.[10] It crystallized from dilute alcohol as fine plates, m.p. 276–80° (decomp.). Found: N, 6·2%. $C_{35}H_{56}O_9N_3Cl$ requires: N, 6·0%.

Peruvosidic acid (*IV*).—This was obtained by the action of chromic acid in glacial acetic acid on peruvoside in the cold employing enough reagent to provide just over one equivalent of oxygen according to the method described by Hegedus *et al.*[11] The acid crystallized from aqueous alcohol as colourless prisms, m.p. 226–28° (decomp.). Legal reaction: positive,

Al-Hg or
NaBH4
CrO3
HS (CH2)nSH;
Raney Ni
I
II
III
IV
Thevetose

$[\alpha]_D^{29} = -57° \pm 3°$ ($c = 0{\cdot}763$ in methanol). Found: C, 63·0; H, 8·2; $-OCH_3$, 5·6%. $C_{30}H_{44}O_{10}$ (IV) requires: C, 63·8; H, 7·9; $-OCH_3$ (1), 5·5%.

Peruvosidic acid methyl ester prepared by the action of ethereal diazomethane on peruvosidic acid in methanol crystallized from acetone-ether as colourless short needles, m.p. 130–34°. $[\alpha]_D^{29} = -25{\cdot}6° \pm 3°$ ($c = 0{\cdot}651$ in methanol). Found: C, 63·4; H, 8·2; $-OCH_3$, 10·8%. $C_{31}H_{46}O_{10}$ requires: C, 64·3; H, 8·0; $-OCH_3$ (2), 10·7%.

Ruvoside (*III*).—It crystallized from methanol-ether as colourless prisms, m.p. 228–30°. It gave positive Molisch and Legal reactions and a negative Keller-Kiliani reaction. Colour with conc. sulphuric acid: pale yellow-pink-deep pink-rose. $[\alpha]_D^{27} = -57{\cdot}8° \pm 3°$ ($c = 0{\cdot}663$ in methanol). Found: C, 64·4; H, 8·4; $-OCH_3$, 5·8%. $C_{30}H_{46}O_9$ (III) requires: C, 65·4; H, 8·4; $-OCH_3$ (1), 5·6%.

Lactone titration.—Ruvoside (20·1 mg.) was refluxed with 0·1 N alcoholic potash (10 ml.) for 2 hours and titrated with 0·1 N sulphuric acid using phenolphthalein as indicator. A blank experiment was simultaneously done. Alkali consumed: 0·401 ml. of 0·1 N alkali, corresponding to 1·1 lactone group.

Ruvoside acetate.—Ruvoside was acetylated with pyridine and acetic anhydride in the cold. The acetate could not be satisfactorily crystallized. By dissolving it in a small quantity of acetone and adding absolute ether a microcrystalline powder, m.p. 110–22° was obtained. Colour with conc. sulphuric acid: yellow-orange-pink. $[\alpha]_D^{27} = -35{\cdot}8° \pm 2°$ ($c = 0{\cdot}922$ in chloroform). Found: C, 63·5; H, 7·7; $-COCH_3$, 18·3%. $C_{36}H_{52}O_{12}$ requires: C, 63·9; H, 7·7; $-COCH_3$ (3), 19·1%.

Isoruvoside prepared by the action of cold methyl alcoholic potash on ruvoside as described earlier[8] crystallized from methyl alcohol as colourless needles, m.p. 234–37°. Legal reaction: negative. Found: C, 65·0; H, 9·0. $C_{30}H_{46}O_9$ requires: C, 65·4; H, 8·4%.

Isoruvoside acetate.—Isoruvoside was acetylated with pyridine and acetic anhydride at room temperature. The product crystallized from acetone-ether as fine short needles, m.p. 197–200°. Found: C, 63·7; H, 8·2; $-COCH_3$, 18·3%. $C_{36}H_{52}O_{12}$ requires; C, 63·9; H, 7·7; $-COCH_3$ (3), 19·1%.

Hydrolysis of ruvoside.—Ruvoside (300 mg.) was treated with Kiliani's mixture[12] (10 ml.) (acetic acid: conc. hydrochloric acid: water, 7:2:11)

and heated for 50 mts. in a boiling water-bath. The yellow solution was cooled and left in the ice-chest for 18 hours when a viscous layer settled down. The supernatant liquid was transferred to a separating funnel and the viscous layer washed with small quantities of water which were transferred to the separating funnel. The aqueous liquid was extracted with chloroform and the extracts after washing with a little water, 2 N sodium carbonate and water were mixed with the viscous layer, the chloroform solution dried over sodium sulphate and the solvent removed under vacuum. The residue (195 mg.) was chromatographed over alumina when two crystalline sugar-free fractions (negative Molisch test) melting at 228–30° and 169–72° were obtained in small yields. These fractions have not been characterized.

The aqueous liquid and the first wash-water described above were mixed and worked up for the sugar moiety as described by Rheiner *et al.*[13] under the hydrolysis of odoroside-H-monoacetate. The sugar crystallized from acetone-ether as colourless needles, m.p. 126–29°. $[\alpha]_D^{31} = -65{\cdot}8° \pm 3°$ (after 10 mts.) and $-35{\cdot}7° \pm 3°$ (after 14 hours) ($c = 0{\cdot}681$ in water). Found: C, 47·6; H, 8·1; $-OCH_3$, 17·1%. $C_7H_{14}O_5$ requires: C, 47·2; H, 7·9; $-OCH_3$ (1), 17·4%.

Mixed m.p. with authentic L-thevetose obtained from neriifolin by Kiliani hydrolysis was undepressed.

Hydrolysis of peruvoside.—Peruvoside was hydrolysed exactly as described under ruvoside. The sugar isolated in the same manner crystallized as colourless needles from acetone-ether, m.p. 125–28°. $[\alpha]_D^{27} = -67{\cdot}2° \pm 2°$ (after 10 mts.) and $-33{\cdot}2° \pm 2°$ (after 14 hours) ($c = 1{\cdot}366$ in water). Found: C, 47·2; H, 7·8; $-OCH_3$, 17·0%. $C_7H_{14}O_5$ requires: C, 47·2; H, 7·9; $-OCH_3$ (1), 17·4%.

Mixed m.p.s with L-thevetose from neriifolin and from ruvoside were undepressed. On paper chromatogram using the solvent system butanol-pyridine-water[14] authentic thevetose from neriifolin and the sugars from peruvoside and ruvoside behaved exactly alike.

Reduction of peruvoside to ruvoside.—(*a*) Using aluminium-amalgam (method of Rabald and Kraus[15]). The reduction was carried out as per details described by Doebel *et al.*[16] in their experiments on the reduction of α-antiarin to *al*-dihydro-α-antiarin. The reduction product was chromatographed over alumina. The methanol-chloroform eluates containing 1% and 2% of methanol gave unchanged peruvoside (m.p. and mixed m.p.) and the methanol-chloroform eluate containing 5% methanol, on crystalliza-

tion from methanol-ether, yielded ruvoside as colourless prisms, m.p. 232–34°. Colour reactions were same as with natural ruvoside. $[\alpha]_D^{27} = -61{\cdot}5° \pm 3°$ ($c = 0{\cdot}602$ in methanol). Found: C, 65·0; H, 8·5; $-OCH_3$, 5·9%. $C_{30}H_{46}O_9$ requires: C, 65·4; H, 8·4; $-OCH_3$ (1), 5·6%.

Mixed m.p. with natural ruvoside was undepressed. The behaviours of these two samples on paper chromatogram (solvent system: chloroform-formamide) were identical.

(*b*) *Using sodium borohydride* (*method of Hunger and Reichstein*).[17]—The reduction was carried out as per details described by Golab *et al.*[7] in their experiments on the reduction of cannogenin to cannogenol. The reduction product was chromatographed over alumina. Unchanged peruvoside and ruvoside were eluted by the same solvents as in experiment (*a*). The latter crystallized from methanol-ether as prisms, m.p. 232–34°. Colour reactions were identical with natural ruvoside. Mixed m.p. with natural ruvoside was undepressed. $[\alpha]_D^{28} = -59{\cdot}7° \pm 2°$ ($c = 0{\cdot}620$ in methanol).

Note.—Substances for analysis and rotation were dried to constant weight in high vacuum at 110° and 80° respectively.

SUMMARY

The constitution of ruvoside, a new glycoside from *Thevetia neriifolia*, has been shown to be α-L-thevetoside of cannogenol (= 19-hydroxy-neriifolin).

REFERENCES

1. Rangaswami, S. and Venkata Rao, E. — *J. Sci. industr. Res.*, 1958, **17 B**, 331.
2. ———— .. *Ibid.*, 1959, **18 B**, 443.
3. Boehringer, Sohne, C. H. Ingelheim — *Austrian Patent*, 195577 of 1958.
4. Bloch, R., Rangaswami, S. and Schindler, O. — *Helv. Chim. Acta*, 1960, **43**, 652.
5. Chen, K. K. and Steldt, F. A. — *J. Pharmacol. exp. Therap.*, 1942, **76**, 167.
6. Helfenberger, H. and Reichstein, T. — *Helv. Chim. Acta*, 1948, **31**, 1470.
7. Golab, T., Trabert, CH., Jager, H. and Reichstein, T. — *Ibid.*, 1959, **42**, 2418.
8. Smith, S. .. *J. Chem. Soc.*, 1930, 2481.
9. Sigg, H. P., Tamm, Ch. and Reichstein, T. — *Helv. Chim. Acta*, 1955, **38**, 176.

10. Schindler, O. and Reichstein, T. *Helv. Chim. Acta*,, 1951, **34**, 521.
11. Hegedus, H., Tamm, Ch. and Reichstein, T. *Ibid.*, 1955, **38**, 98.
12. Kiliani, H. .. *Ber.*, 1930, **63**, 2866.
13. Rheiner, A., Hunger, A. and Reichstein, T. *Helv. Chim. Acta*, 1952, **35**, 687.
14. Sigg, H. P., Tamm, Ch. and Reichstein, T. *Ibid.*, 1955, **38**, 166.
15. Rabald, E. and Kraus, J. .. *Z. Physiol. Chem.*, 1940, **265**, 39.
16. Doebel, K. ,Schlittler, E. and Reichstein, T. *Helv. Chim. Acta*, 1948, **31**, 688.
17. Hunger, A. and Reichstein, T. *Ber.*, 1952, **85**, 635.

LATTICE POINTS OF INDEFINITE QUADRATIC FORMS WITH INTEGRAL COEFFICIENTS

By V. Venugopal Rao

(Department of Mathematics and Statistics, University of Poona, Poona-7)

Received October 17, 1961

(Communicated by Dr. B. S. Madhava Rao, F.A.SC.)

Let S be a rational, symmetric, positive definite matrix with m rows. Let X denote a real column vector with m rows and X', the transpose of X. Further let $S[X] = X'SX$. Let $A(S, t)$ denote the number of integral column vectors X such that $S[X] = t$. As S is assumed to be positive definite, $A(S, t)$ is necessarily finite. The lattice point problem associated with the quadratic form $S[X]$ is concerned with the determination of an asymptotic formula for the function $\sum_{0<t<x} A(S, t)$, as $x \to \infty$ together with an estimate for the error term. It is well known that

$$\sum_{0 \leqslant t \leqslant x} A(S, t) = |S|^{-1/2} \frac{\pi^{m/2}}{\Gamma\left(\frac{m}{2}+1\right)} x^{m/2} + P(S, x),$$

with $P(S, x) = o(x^{m/2})$ as $x \to \infty$; $|S|$ being the determinant of S. Landau[1] has shown that $P(S, x) = O(x^{m/2-m/m+1})$, for $m \geqslant 2$ and this result has been improved by several others. In particular for $m > 4$, it is known that $P(S, x) = O(x^{m/2-1})$ and further that this estimate is the best for $m > 4$; a result which can be expressed by writing $P(S, x) = \Omega(x^{m/2-1})$, Ω being the Hardy-Littlewood symbol.

Our aim here is to seek analogues of the above-mentioned results (for $m > 4$) for indefinite quadratic forms. In the case of an indefinite matrix S, $A(S, t)$ is, in general, infinite. Siegel, in his researches on the analytical theory of quadratic forms, has discovered an analogue of $A(S, t)$ for S rational and indefinite. *We now assume that S is a rational, symmetric, non-singular, indefinite matrix with m rows.* Siegel, more generally, considers rational solutions Y of the matrix equation $S[Y] = t$ (t being a rational number), with $Y \equiv A \pmod 1$, A being a fixed rational column vector with m rows, and has defined an arithmetical function $M(S, A, t)$. $M(S, A, t)$ is always finite except in the cases when either $m = 4$, $t = 0$,

$|S|$ the square of the rational number or $m = 3$, $-t|S|$ the square of a rational number. If S is positive definite,

$$M(S, A, t) = \rho_{m-1} |S|^{-m/2} t^{1-m/2} \frac{A(S, A, t)}{E_A(S)},$$

where $A(S, A, t)$ denotes the number of rational column vectors $Y \equiv A \pmod 1$ such that $S[Y] = t$; $E_A(S)$ denotes the number of unimodular matrices U of order m satisfying $S[U] = S$ and $UA \equiv A \pmod 1$. Further

$$\rho_{m-1} = \prod_{k=1}^{m-1} \frac{\pi^{k/2}}{\Gamma\left(\frac{k}{2}\right)}.$$

The precise definition of $M(S, A, t)$ can be found in (3).

Let S be a semi-integral, symmetric, non-singular, indefinite matrix with m rows and A a rational column vector with m rows such that $2SA$ and $S[A]$ are integral. Let $\Gamma_A(S)$ denote the group of unimodular matrices of order m such that $S[U] = S$ and $UA \equiv A \pmod 1$. Let $\mu_A(S)$ denote the measure of the group $\Gamma_A(S)$ in the sense of Siegel.[3] Then we prove the following:

THEOREM: Let

$$m > 4 \text{ and } \sum_{0<t\leqslant x} M(S, A, t) = \mu_A(S)\, x + P(S, A, x).$$

Then

$$P(S, A, x) = O(1), \tag{1}$$

and

$$P(S, A, x) = \Omega(1), \tag{2}$$

as $x \to \infty$.

The proof of the above theorem is similar to that of a corresponding result of Walfisz[2] valid for S rational and positive definite. The proof of the result of Walfisz makes use of a generalization of an asymptotic formula for $A(E, t)$, E being the unit matrix of order m ($m > 4$). Hardy has shown that the error term in the asymptotic formula for $A(E, t)$ vanishes if $m \leqslant 8$; so that one has an exact formula for $A(E, t)$ in terms of the so-called "Singular series". Siegel has proved an exact formula for $M(S, A, t)$ for $m > 4$ and our proof is based on this fundamental result of Siegel.

By the main theorem of Siegel[8] we have

$$\frac{M(S, A, t)}{\mu_A(S)} = \sum_{q=1}^{\infty} \sum_{\substack{0 \le p/q \le 1 \\ (p,q)=1}} \frac{G(S, p, q)}{q^m} e^{-2\pi i t p/q}, \tag{3}$$

with the Gaussian sum,

$$(4)\quad G(S, p, q) = \sum_{X \pmod q} e^{2\pi i S[X+A] p/q}, \tag{4}$$

the summation on the right of (4) being over the set of residue classes of integral vectors with m rows, modulo q. For $m > 4$, the series on the right of (3) is absolutely convergent. We single out the term with $q = 1$ on the right side of (3) and sum over all integers t such that $0 < t \leqslant x$. We then have,

$$\frac{1}{\mu_A(S)} \sum_{0<t\leqslant x} M(S, A, t)$$

$$= x - B + \sum_{q=2}^{\infty} \sum_{\substack{0 \le p/q \le 1 \\ (p,q)=1}} \frac{G(S, p, q)}{q^m} \sum_{0<t\leqslant x} e^{-2\pi i t p/q}$$

where

$$B = x - [x] < 1.$$

Now

$$\left| \sum_{q=2}^{\infty} \sum_{\substack{0 \le p/q \le 1 \\ (p,q)=1}} \frac{G(S; p, q)}{q^m} \sum_{0<t\leqslant x} e^{-2\pi i t p/q} \right| \leqslant$$

$$\sum_{q=2}^{\infty} \sum_{\substack{0 \le p/q \le 1 \\ (p,q)=1}} \frac{|G(S; p, q)|}{q^m} \left| \sum_{0<t\leqslant x} e^{-2\pi i t p/q} \right|. \tag{5}$$

It is known (3, p. 37) that

$$|G(S, p, q)| < (2 \| S \| q)^{m/2} \tag{6}$$

where $\| S \|$ denotes the absolute value of $|S|$. For $q > 2$, $k > 1$, we have the estimate (4, p. 23, Lemma 6),

$$\left| \sum_{t=1}^{k} e^{-2\pi i t p/q} \right| < \text{Max.} \left(\frac{q}{p}, \frac{q}{q-p} \right) = \lambda(p, q) \quad \text{(say)}. \tag{7}$$

Then (5) is majorized by:

$$2^{m/2} \| S \|^{m/2} \sum_{q=2}^{\infty} \sum_{\substack{0 \leq p/q < 1 \\ (p,q)=1}} \frac{\lambda(p,q)}{q^{m/2}}. \tag{8}$$

Now (8) is majorized by

$$2^{m/2+1} \| S \|^{m/2} \sum_{q=2}^{\infty} \frac{1+\log q}{q^{m/2-1}}$$

$$= O(1), \quad \text{for} \quad m > 4.$$

With this, (1) is proved.

For the proof of (2), let, $0 < \delta < 1$.

Then for x integral

$$\sum_{0<t\leq x} M(S, A, t) = \sum_{0<t\leq x+\delta} M(S, A, t);$$

or what is the same.

$$P(S, A, x+\delta) - P(S, A, x) = -\delta\mu_A(S). \tag{9}$$

If $P(S, A, x) = o(1)$, then $P(S, A, x+\delta) - P(S, A, x) = o(1)$ in contradiction to (9). Hence $P(S, A, x) = \Omega(1)$ as $x \to \infty$.

References

1. Landau, E. .. "Zur analytischen Zahlentheorie der definiten quadratischen Formen (Über die Gitterpunkte in einem mehrdimensionalen Ellipsoid)," *Berliner Akademie-berichte*, 1915, 458–76.
2. Walfisz, A. .. "Über Gitterpunkte in mehrdimensionalen ellipsoiden," *Math. Zeit.*, 1924, **19**, 300–07.
3. Siegel, C. L. .. "Idefinite quadratische Formen und Funktionentheorie—I, *Math. Annalen.*, 1951, **124**, 17–54.
4. Vinogradov, I. M. .. *The Method of Trigonometrical Sums in the Theory of Numbers*, Interscience Publishers, London and New York.

845–61. Printed at the Bangalore Press, Bangalore City, by T. K. Balakrishnan, Superintendent, and Published by The Indian Academy of Sciences, Bangalore.

Supplement to the
"Proceedings of the Indian Academy of Sciences"

INDEX TO VOL. LIV—(A)

AUTHORS' INDEX

Brahm Dev and Jain, B. D. — Gravimetric determination of uranium and thorium with 1-hydroxy-xanthone, 341.

Broida, H. P. .. *See* Krishnamachari and others.

Chiplonkar, V. T. and Naik, P. K. — Electrical oscillations in a constricted D.C. cold-cathode glow discharge with a three electrode system, 80.

Degaonkar, S. S. .. Changes in the electron density distribution in the ionosphere over Ahmedabad associated with solar flares and magnetic storms, I, 24.

Dharmatti, S. S., Govil, G., Kanekar, C. R., Khetrapal, C. L. and Virmani, Y. P. — High resolution NMR spectra of some tri-substituted benzenes, 331.

Govil, G. .. *See* Dharmatti and others.

Jain, B. D. .. *See* Brahm Dev and Jain.

Jha, Sudhanshu S. .. Nuclear magnetic resonance spectra for a system ABC of spin $\frac{1}{2}$ nuclei and their linewidths, 13.

John, Joseph, P. and Shanmugam, P. — Heterocyclic compounds, XVII, 161.

Kanekar, C. R. .. *See* Dharmatti and others.

Kapur, J. N. .. On the existence and uniqueness of flows behind three-dimensional curved stocks, 116.

Khetrapal, C. L. .. *See* Dharmatti and others.

Krishnamachari, S. L. N. G., Nicholls, R. W. and Broida, H. P. — Emission spectra from solids condensed at very low temperatures from the electrical discharge products of nitrogen-carbon monoxide and nitrogen-acetylene mixtures, 61.

Krishnan, K. .. Raman spectra of organic compounds, II, 89.

Krishnan, M. .. Heterocyclic compounds, XVIII, 165.

Naik, P. K. ..	*See* Chiplonkar and Naik.
Narayan, R. and Venkatesan, V. K.	Tensammetric studies of thiourea and its derivatives, 109.
Nicholls, R. W. ..	*See* Krishnamachari and others.
Puranik, P. G. and Venkata Ramiah, K.	The infra-red and Raman spectroscopic studies of amides, 69.
	Spectroscopic studies of the associations of heterocyclic amines (2-amino-methyl pyridines and amino-quinolines), 121.
	Raman and infra-red spectra of amines. Toluidines and *para*-amino-acetophenone, 146.
Radhakrishnamurti, P. S. ..	Kinetic studies in ester hydrolysis, XI, XII, 36, 325.
Rajeswari (Miss), G. K. ..	Flow of non-Newtonian fluid between torsionally oscillating discs, 188.
Raman, C. V. ..	The vibrations of the MgO crystal structure and its infra-red absorption spectrum, I, II, III, IV, 205, 223, 233, 244.
	The spectroscopic behaviour of rock-salt and the evaluation of its specific heat, I, II, III, IV, 253, 266, 281, 294.
Raman, R. and Soundararajan, Sundaresa	Dipole moments and molecular structure of picrates of aromatic hydrocarbons and heterocyclic amines, 41.
Rangaswami, S. and Rao, E. Venkata	Anthoxanthin pigments of the leaves of *Digitalis lanata* Ehrh. and the constitution of a new pigment dination, 51.
	Constitution of Ruvoside, 345.
Rangaswami, S. and Sambamurthy, K.	Chemical examination of the leaves of *Rhododendron cinnamomeum*, 99.
	Constitution of campanulin, 132.
Rao, B. D. Nageswara and Venkateswarlu, P.	The nuclear magnetic resonance spectra of four spin systems, II, III, 1, 305.
Rao, E. Venkata ..	*See* Rangaswami and Rao.
Rao, N. V. Subba and Sundaramurthy, V.	Search for physiologically active compounds, IV, V, 105, 321.

Rao, V. Venugopal .. Lattice points of indefinite quadratic forms with integral coefficients, 352.

Rastogi, R. G. .. Some effects of geomagnetic activity on the F2 region of the ionosphere over Leopoldville (4·4° S., 15·3° E.), 155.

Sambamurthy, K. .. *See* Rangaswami and Sambamurthy.

Sastry, N. P. and Thosar, B. V. Decay-time of scintillations in CsI (Tl) crystal, 140.

Shanmugam, P. .. *See* John and Shanmugam.

Sinha, K. P. .. An approximate method for the calculation of the incompressible laminar spanwise boundary layer on an infinite uniform yawed cylinder with distributed suction, 171.

Soundararajan, Sundaresa .. *See* Raman and Soundraarajan.

Sundaramurthy, V. .. *See* Rao and Sundaramurthy.

Thosar, B. V. .. *See* Sastry and Thosar.

Venkata Ramiah, K. .. *See* Puranik and Venkata Ramiah.

Venkatesan, V. K. .. *See* Narayan and Venkatesan.

Venkateswarlu, P. .. *See* Rao and Venkateswarlu.

Virmani, Y. P. .. *See* Dharmatti and others.

TITLE INDEX

Campanulin, constitution of (Rangaswami and Sambamurthy), 132.

CsI (Tl) crystal, decay-time of scintillations in (Sastry and Thosar), 140.

Digitalis lanata Ehrh., anthoxanthin pigments of the leaves of, and the constitution of a new pigment dination (Rangaswami and Rao), 51.

Dipole moments and molecular structure of picrates of aromatic hydrocarbons and heterocyclic amines (Raman and Soundararajan), 41.

Electrical oscillations in a constricted D.C. cold-cathode glow discharge with a three electrode system (Chiplonkar and Naik), 80.

Electron density distribution in the ionosphere over Ahmedabad, changes in the, associated with solar flares and magnetic storms, I (Degaonkar), 24.

Emission spectra from solids condensed at very low temperatures from the electrical discharge products of nitrogen-carbon monoxide and nitrogen-acetylene mixtures (Krishnamachari and others), 61.

Flow of non-Newtonian fluid between torsionally oscillating discs (Rajeswari), 188.

Flows behind three-dimensional curved stocks, the existence and uniqueness of (Kapur), 116.

Geomagnetic activity, some effects of, on the F2 region of the ionosphere over Leopoldville (4·4° S., 15·3° E.) (Rastogi), 155.

Heterocyclic amines (2-amino-methyl pyridines and amino-quinolines), the associations of, spectroscopic studies of the, (Puranik and Venkata Ramiah), 121.

Heterocyclic compounds, XVII (John and Shanmugam), 161; XVIII (Krishnan), 165.

Infra-red and Raman spectroscopic studies of amides (Puranik and Venkata Ramiah), 69.

Kinetic studies in ester hydrolysis, XI, XII (Radhakrishnamurti), 36, 325.

Laminar spanwise boundary layer, incompressible, on an infinite uniform yawed cylinder, with distributed suction, an approximate method for the calculation of (Sinha), 171.

Lattice points of indefinite quadratic forms with integral coefficients (Rao), 352.

MgO crystal structure, the vibrations of, and its infra-red absorption spectrum, I, II, III, IV (Raman), 205, 223, 233, 244.

NMR spectra, high resolution, of some tri-substituted benzenes (Dharmatti and and others), 331,

Nuclear magnetic resonance spectra for a system ABC of spin ½ nuclei and their linewidths (Jha), 13.

Nuclear magnetic resonance spectra of four spin systems, II, III (Rao and Venkateswarlu), 1, 305.

Physiologically active compounds, search for, IV, V (Rao and Sundaramurthy), 105, 321.

Raman and infra-red spectra of amines. Toluidines and *para*-amino-acetophenone (Puranik and Venkata Ramiah), 146.

Raman spectra of organic compounds, II (Krishnan), 89.

Rhododendron cinnamomeum, leaves of, chemical examination of (Rangaswami and Sambamurthy), 99.

Rock-salt, the spectroscopic behaviour of, and the evaluation of its specific heat, I, II, III, IV (Raman), 253, 266, 281, 294.

Ruvoside, constitution (Rangaswami and Rao), 345.

Thiourea and its derivatives, tensammetric studies (Narayan and Venkatesan), 109.

Uranium and thorium, gravimetric determination of, with 1-hydroxy-xanthone, (Brahm Dev and Jain), 341.

NOTICE TO AUTHORS

Scientific papers intended for publication in the *Proceedings of the Indian Academy of Sciences* can be accepted only when they are communicated by a Fellow of the Academy whose duty shall be to satisfy himself that such communications are fit to be read at the Meeting of the Academy and published in its *Proceedings*.

Papers should not ordinarily exceed fifty pages of foolscap. MSS. should be either typewritten or written in legible hand on one side of the paper. All papers should be carefully revised by the authors and should be absolutely in final form for printing. Position for text-figures should be indicated. Each paper shall conclude with a critical summary not exceeding 350 words.

Drawings, diagrams or other illustrations should be made on larger scale (preferably) twice the size than the ones in which they are intended to appear. They should be done in Indian ink on bristol board with lettering in pencil. Scale of magnification of camera lucida tracings should be indicated by the side of drawings. In certain special cases arrangements will also be made for monochrome lithographic and other colour plates. Reduction of illustrations desired should be indicated in pencil. Appropriate legends should accompany all drawings. Names of authors are to be marked in pencil on the left-hand corner of drawing sheets. Photomicrographs should be securely mounted with colourless paste.

All tables, quotations and footnotes which will be set hereafter (beginning from Vol. I, No. 2) in types smaller than the text, should be typewritten on separate sheets and placed with the text in proper sequence. Footnotes should be numbered in Arabic numerals.

References to literature in the text should be given, whenever possible, in chronological order, only the names of authors and years of publication, in brackets, being given. They should be cited in full after the summary, the authors' names following in alphabetical order. Thus,

Name or Names of author; Name of Journal (abbreviation) with a single underline; Year of publication; Number of Volume with a double underline, and lastly page. The following would be a useful illustration:—

Bergmann and Stather . . . . . Z. Physiol. Chem., 1926, 152, 189.

Two copies of slip-proof and wherever possible, a page proof for final revision will be sent to authors. All corrections are best made on the slip-proof which should be transmitted to the Office of the Academy. All proof corrections involve heavy expenses which would be negligible if the papers are carefully revised by the authors before submission.

Fifty free reprints including plates and with cover will be supplied for each paper. Additional copies can be supplied at cost on previous intimation.

Blocks appearing in the *Proceedings* will be available for purchase by their respective authors. Orders for the same should be sent along with the corrected proofs and in any case not later than one month after the date of publication of the paper. The price charged would be 25% of the actual cost of the blocks *plus* freight and despatching charges. If the blocks are reproduced in other journals or publications, due acknowledgment should be made in them to the *Proceedings*.

The original drawings and plates of blocks appearing in the *Proceedings* will be returned to such of the authors as may require them provided the cost of despatching such originals is borne by them.

CONTENTS

PAGE

The Nuclear Magnetic Resonance Spectra of Four Spin Systems. III. Proton Resonance Spectra of α, β and γ Picolines . . . . . B. D. Nageswara Rao and Putcha Venkateswarlu 305

Search for Physiologically Active Compounds. Part V. Synthesis of Nitro Coumarins . . . . . N. V. Subba Rao and V. Sundaramurthy 321

Kinetic Studies in Ester Hydrolysis. Part XII. The Alkaline Hydrolysis of Succinates in Mixed Solvents Study of Consecutive Reactions . . . . . P. S. Radhakrishnamurti 325

High Resolution NMR Spectra of Some Tri-Substituted Benzenes . . . . . S. S. Dharmatti, G. Govil, C. R. Kanekar, C. L. Khetrapal and Y. P. Virmani 331

Gravimetric Determination of Uranium and Thorium with 1-Hydroxy-Xanthone . . . . . Brahm Dev and B. D. Jain 341

Constitution of Ruvoside . . . . S. Rangaswami and E. Venkata Rao 345

Lattice Points of Indefinite Quadratic Forms with Integral Coefficients . . . . . V. Venugopal Rao 352

1510